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The synthesis and use of amine functionalized polyaryletherketones in tough thermoset formulations/

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THE SYNTHESIS AND USE OF AMINE FUNCTIONALIZED POLYARYLETHERKETONES IN TOUGH THERMOSET FORMULATIONS

A Dissertation Presented

By

Samuel A. Thompson

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Polymer Science and Engineering

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of Amine Functionalised Polyaryletherketones
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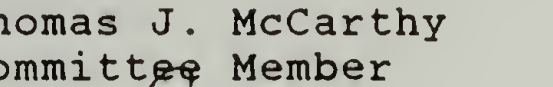

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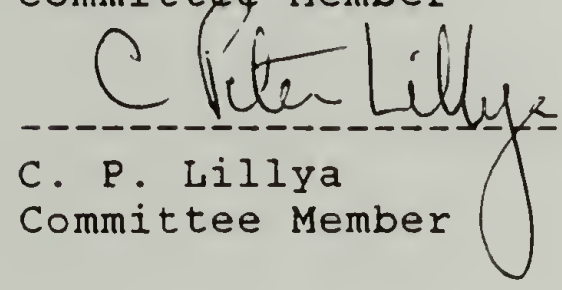

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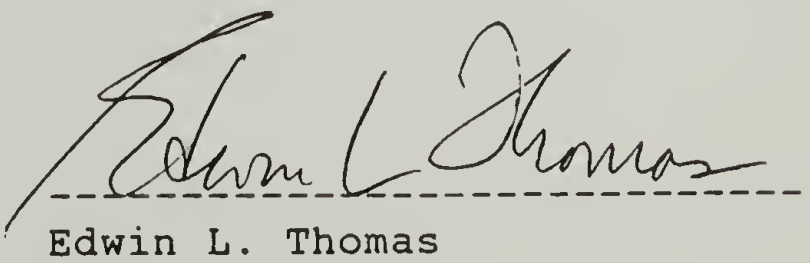

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ABSTRACT

THE SYNTHESIS AND USE
OF AMINE FUNCTIONALIZED POLYARYLETHERKETONES
IN TOUGH THERMOSET FORMULATIONS

February 1988)

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A study of the synthesis and use of primary aromatic amine functionalized polyaryletherketones in high performance applications is presented. Homopolymers synthesized via the condensation reaction of 4,4´-difluorobenzophenone with bisphenol A, hydroquinone, methylhydroquinone, tertiarybutylhydroquinone and resorcinol were used in thermosetting co-networks with epoxy resins. The resulting resin formulations were characterized for processability as determined by B-stagability, and the presence of tack and drape in the B-stage at room temperature. Mechanical property characterization of the cured resins included measurement of the critical stress intensity factor and strain energy release rate for mode one crack propagation. The dynamic mechanical properties of the cured resins were measured on a Dynastat dynamic mechanical testing machine , from which the glass transition temperature was obtained. The resistance to water, methylene chloride, methyl ethyl ketone, jet fuel, deicing fluid and Skydrol hydraulic

fluid was also determined. Scanning electron microscopy of fracture surfaces as well as transmission electron microscopy of bulk material was performed.

It was observed that the incorporation of amine functionalized bisphenol A, tertiarybutylhydroquinone, and resorcinol based polyaryletherketones into various commercial epoxy resins cured with diaminodiphenylsulphone or methylenedianiline resulted in extremely fracture resistant resins. At low weight percent polyaryletherketone incorporation a phase separation was observed in which the inclusions were polyaryletherketone rich and the matrix epoxy rich. At these low loading levels small increases in toughness over the neat epoxy resin were obtained. At higher loading levels a phase inversion was observed in which the matrix is now polyaryletherketone rich. At these high loading levels increases in fracture resistance of up to eight times were obtained. Increased resistance of these modified resins to polar solvents was also observed.

The crosslinking of commercially available hydroquinone based polyaryletherketone (Victrex PEEK) was also investigated using a novel technique for introducing short, stiff, diimine crosslinks. Increases in the glass transition temperature of Victrex Peek by 140°C were obtained.

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CHAPTER 1

INTRODUCTION TO HIGH PERFORMANCE COMPOSITE MATERIALS

The technology of composite materials is perhaps as old as man himself. Archaeologists have found that early civilizations frequently used manmade composite structures in the construction of hunting utensils and shelter. Despite the apparent age of this science, the greatest achievements in composite materials have been attained in the last 30 years. It was not until the early 1960's that modern fibrous reinforcement materials were developed. The first of these fibrous materials was made from boron followed subsequently by graphite (1). Composite materials reinforced with these fibers have been developed to replace the more conventional structural materials such as steel, aluminum and wood in applications where improvements in material performance, specific strength, specific stiffness, environmental resistance, cost effectiveness or processing are needed. In the past 20 years there has been increased interest in the development of composite structures which can withstand environmental extremes with a minimum of damage. The motivation for this interest stems largely from the need for materials for aerospace applications. The environmental extremes encountered in these applications may include high temperature, high stress, corrosive solvents and impact. The intense effort in the development of

lightweight composite materials for this area has been fueled by the potential for weight savings in structural applications where operation cost and performance are strong functions of unit mass. Composite materials designed to operate in these extremely rigorous environments are generally referred to as high performance composites. While suitable materials for fibrous reinforcement, which impart stiffness to the composite are commercially available, there are very few composite matrix materials which are capable of performing in these rigorous conditions. The properties which are desirable in a high performance composite matrix material include: a high fracture energy, a high modulus, a high glass transition temperature, good solvent resistance, good adhesion to the fibrous reinforcement, and above all processability. A high fracture energy is necessary to prevent growth of intrinsic or damage initiated flaws in the material, allowing for the attainment of maximum weight savings. A high tensile modulus, usually in the region of 2.5 to 4 Gigapascals, is required to maximize the specific stiffness imparted by the fibrous reinforcement. A high glass transition temperature is necessary since it is this parameter which often determines the upper use temperature of the composite. Good resistance to the absorption of the solvents that will be encountered in service reduces the drop in mechanical performance which usually accompanies swelling. Good adhesion must exist between the matrix and the fiber to allow for adequate stress transfer to the

fibers, the main stress bearing components. The most important property of the matrix material is that it be processable using conventional prepreg technology. This technology requires that the material be in a state of low viscosity in which fibers can be coated efficiently. After coating the fibers, these prepregs must have sufficient tack and drape at room temperature to allow for layup of the plys (2). Tack refers to the adhesive nature of the individual prepreg plys and drape refers to the flexibility of these plys.

Historically manufacturers have looked to thermosetting matrix materials for use in high performance composites (3). Until recently the most popular matrix resins were those based upon epoxide chemistry. While these resins satisfy most of the property requirements for a high performance composite matrix, each suffer from brittleness and water sensitivity (4,5,6). As a result of the high crosslink density required to achieve a high glass transition temperature in these resins they lack the ability to undergo the molecular motion in response to stress which is required for ductility (7). These materials exhibit brittle failure at critical stress levels which tend to be quite low. As a result of the hydroxyl groups created during an amine cure, these epoxy matrix materials are extremely hydrophillic, absorbing several percent by weight of water upon exposure

to humid environments (8,9). This water absorption results in an increase in molecular motion of the matrix in response to applied stress leading to a considerable drop in modulus and glass transition temperature (10).

Recently investigators have turned toward the use of aromatic chain thermoplastic materials in high performance composite applications (6). While these thermoplastic materials are much tougher and water resistant than those based upon epoxide chemistry they all lack ease of processing. Composite manufacturing from these materials involves the use of solvents and/or high melting temperatures (11,12). Prepreg sheets of these materials lack tack and drape below their glass transition temperature and therefore cannot be processed using conventional prepreg technology. The more popular of these aromatic thermoplastic materials include the polyetherethersulphone made from bisphenol A and 4-chlorophenylsulphone and the polyetheretherketone made from hydroquinone and 4,4'-difluorobenzophenone. The former is an amorphous polymer having a glass transition temperature of 225°C while the latter is a semicrystalline polymer having a glass transition temperature of 143°C and a crystalline melt temperature of 325°C (13).

In response to the deficiencies of these two types of materials (brittle and water sensitive thermosets on the one hand and improcessable aromatic thermoplastics on the other), a novel approach has recently been taken to

incorporate the best properties of both of these two material types. This approach is very similar to that taken in the toughening of low glass transition temperature (<120° C) epoxy resins with carboxy- or amine-terminated butadiene acrylonitrile rubbers (14-16). The rubber toughened systems are characterized by initial miscibility of the epoxy resin and the functionalized rubber followed by phase separation during cure into an epoxy rich phase and a rubber rich phase, between which covalent bonding is possible (17-19). At loading levels of less than 20% by weight rubber the phase separated morphology consists of an epoxy rich continuous phase with rubber rich inclusions. These rubber rich inclusions act as stress concentrators ahead of a crack tip such that extensive localized shear yielding of the continuous phase occurs (20). During deformation the rubber inclusion also undergoes cavitation or matrix debonding which act to relieve the plane strain (triaxial stress) condition at the crack tip, facilitating further shear yielding (20,21).

Unfortunately the mechanism of rubber toughening in low glass transition temperature epoxy resins does not improve fracture resistance significantly in higher glass transition formulations. Much controversy surrounds the reason for this inability to toughen, however it seems to be the result of the high crosslink density required to achieve a high

glass transition temperature. The high crosslink density of the network reduces molecular mobility inhibiting localized shear yielding, leading to the absorption of much less energy prior to catastrophic failure (7,22).

In the recently developed approach, which combines the desirable properties of the thermoset and aromatic thermoplastic materials, an end functionalized oligomeric aromatic thermoplastic is reacted into a high glass transition temperature epoxy resin system. This system is similar to the rubber toughened system in that it can be characterized by initial miscibility followed by phase separation during cure (23-26). Unlike the rubber toughened systems, the weight percent of end functionalized oligomer is loaded at a level sufficient to cause a phase inversion (23). This phase inverted system consists of a lightly crosslinked aromatic thermoplastic rich continuous phase with epoxy rich inclusions. In this morphology the material exhibits toughness and water resistance which approaches that of the high molecular weight aromatic thermoplastic homopolymer, while attaining a high level of processability (27).

Pioneering work in this area was carried out on phenol terminated polyethersulphone (28). Later developments involved the use of aromatic amine terminated polyethersulfone, a system for which no catalyst is required (23,24). McGrath investigated the use of higher molecular weight oligomeric amine functionalized polyethersulphone

(23,25,26). In his work considerably improved fracture resistance was obtained. Researchers at Hercules Inc. also investigated the use of amine functionalized polyethersulphone (24). In this work oligomers of less than 5,000 Mn were used at up to 40% by weight in Heloxy 69. These systems attained far superior levels of toughness to that obtained by McGrath. While in each case a tougher matrix material was developed (with the exception of the work done by Hercules Inc.), little emphasis was placed upon the development of a material which is processable, having tack and drape at room temperature.

The approach taken in this dissertation to the development of a tough matrix resin formulation utilizes the technique pioneered by McGrath and Hercules Inc. In this case the approach emphasizes the development of an improved matrix material which is processable along with the development of an improved understanding of the mechanism by which these enhanced mechanical properties are attained. The aromatic thermoplastic polymers investigated are the aromatic amine terminated polyaryletherketones synthesized from various diphenols and 4,4'-difluorobenzophenone. The diphenols investigated include bisphenol A, hydroquinone, methylhydroquinone, tertiarybutylhydroquinone, and resorcinol. Work with the bisphenol A polyaryletherketone in this application was reported by McGrath et al while this dissertation was in progress (29). The specifics of this work will be reviewed in Chapter 2. Since these end

functionalized oligomers are not commercially available they were synthesized in our laboratory. The polyaryletherketones were chosen for several reasons. No work with these polymers in this application had been reported in the literature prior to the initiation of this project. These polymers are also fairly easy to synthesize in the molecular weight range desired from commercially available, inexpensive monomers. The polymer backbone could also be easily regulated via substitution of various diphenols leading to excellent control over the morphology of the polymer produced. These oligomeric end functionalized polymers were dissolved into commercial epoxy resins at 10 to 50 percent by weight. The stoichiometry of this modified epoxy system was maintained through the use of low molecular weight, commercially available, aromatic diamines. Several epoxy resins were initially evaluated to obtain a resin having a solubility parameter / cure morphology such that; a). the end functionalized polyaryletherketones were initially miscible with the epoxy resin at a reasonable prereaction temperature and b). phase separation occurred during cure. It was important to obtain a system which allowed for phase separation into domain sizes which were appropriate for composite use. Obviously, macroscopic phase separation could not be tolerated. The oligomers were functionalized only on the ends to allow for the greatest distance between crosslinks. The greater the distance between crosslinks the greater the ductility of the

matrix material. Since these aromatic thermoplastic polymers are characterized by sufficiently high glass transition temperatures without any crosslinking it was not expected that the glass transition temperature would be a strong function of the molecular weight between crosslinks in the modified resin. The oligomers were functionalized with primary aromatic amines to achieve B-stagability. The primary aromatic amines are characteristically much more reactive than the secondary aromatic amines formed when reaction with one epoxide group occurs (8). The secondary aromatic amine formed is more basic than the primary aromatic amine, however it is also sterically hindered leading to lower nucleophilicity. When the primary aromatic amine is reacted with an epoxy resin at a reasonable temperature for a limited amount of time, the product is almost exclusively a linear polymer; very little crosslinking occurs. This lack of crosslinking is the result of the much lower reactivity of the secondary aromatic amine. The aromatic amine is preferred over the aliphatic amine for three reasons: First, the aliphatic primary amine is much more reactive (nucleophillic) than the primary aromatic amine and therefore would react much faster at the temperatures required for dissolution of the oligomer (30). Second, the secondary aliphatic amines formed during reaction of the primary aliphatic amine with the epoxy resin are much more nucleophillic than the initial primary alliphatic amine which results in extensive crosslinking

immediately and therefore no B-stagability (8). Third, the aliphatic groups in these amines result in a much more flexible linkage, and subsequently, a lower glass transition temperature system.

Although this dissertation is principally an engineering work, each chapter gives an extensive report of the synthetic procedures used to allow for reproduction by future researchers. In actuality, approximately 60% of the time spent on this dissertation was involved in the synthesis of these materials.

Chapters 2 through 6 have been arranged according to polymer structure. The greatest amount of work has been done with the bisphenol A based polyaryletherketone and therefore the most clear understanding of the toughening mechanism can be developed from the data on this material. This information is presented in chapter 2. Chapters 3 and 4 deal with the use of semicrystalline hydroquinone and methylhydroquinone based polyaryletherketones. Chapters 5 and 6 deal with the use of two amorphous polyaryletherketones. In chapter 7 a novel method for crosslinking Victrex polyetheretherketone is presented. Chapter 8 contains conclusion and future work sections.

CHAPTER 2

BISPHENOL A BASED POLYARYLETHERKETONE AS A MATRIX MODIFIER WITH COMMERCIAL EPOXY RESINS

2.1 Introduction

The polyaryletherketone obtained from the reaction of bisphenol A and 4,4´-difluorobenzophenone is an extremely tough amorphous polymer having a glass transition temperature of 120 degrees centigrade. The structure of this polymer in the amine terminated form is shown in Figure 2.1. This polymer lends itself quite nicely to use as a matrix modifier with commercial epoxy resins as a result of its noncrystalline nature and favorable solubility characteristics.

Previous work with this polymer in this application has been reported by McGrath et al(29). In McGrath´s work it is reported that considerably improved matrix toughness is achieved through the incorporation of amine terminated Bisphenol A based polyetheretherketone (BPAPK) into Epon 828. The BPAPK oligomers investigated had number average molecular weights of 7,000 to 18,000 and were used at a loading level of 15 percent by weight in Epon 828 cured with diamino diphenyl sulphone. McGrath´s work does not discuss the processability of these resin formulations nor do the

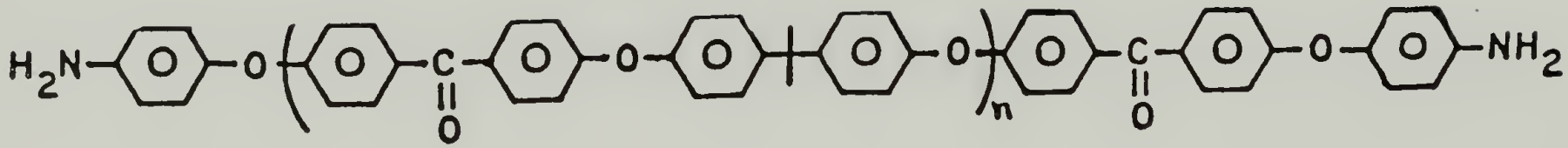


Figure 2.1

BISPHENOL A POLYETHERETHERKETONE

materials attain the extreme levels of toughness that are possible at reasonable molecular weights when loading levels of greater than 15 weight percent are used. It is important to note that McGrath is working at a loading level where the Epon 828 rich phase is continuous and the material is thus incapable of attaining the extreme levels of toughness associated with a BPAPK rich continuous phase. McGrath also uses a solvent dispersal technique for molecular weights of greater than 10,000 grams per mole which is unnecessary. He also reports macroscopic phase separation at higher molecular weights; this can be avoided when the proper epoxy/curing agent combination is used.

In this chapter, an investigation into the synthesis and use of primary aromatic amine terminated BPAPK in formulations with commercial epoxy resins will be reported. The motivations for this investigation were to develop tough, processable, water resistant resin formulations in conjunction with the development of a better understanding of the mechanisms by which these mechanical properties are improved.

2.2 Experimental

Potassium carbonate, potassium hydroxide, bisphenol A, 4,4'-difluorobenzophenone, 4-aminophenol, methylene dianiline (MDA), and diaminodiphenylsulphone (DDS) were obtained from Aldrich Chemical Company in the highest purity

available. Epon 828, Heloxy 69 and My 720 were obtained from Shell, Wilmington Chemical Company and Ciba Geigy respectively. N-methylpyrrolidinone was vacuum distilled from P_2O_5 and stored under nitrogen. Toluene was distilled from CaH_2 and stored under nitrogen.

2.2.1 Synthesis of Oligomeric Aromatic Amine Terminated Polyaryletherketone

Both the polymerization and endcapping reactions are nucleophillic aromatic substitutions (31-33). The potassium carbonate, bisphenol A, and the 4,4′-difluorobenzophenone were added to a 4 neck flask equipped with a mechanical stirrer, thermometer, dean stark trap, nitrogen inlet and outlet, condenser and heating mantle. The flask was purged continuously with nitrogen. N-methylpyrrolidinone (NMP) and toluene were added via cannula. The reaction mixture was slowly heated to a stable reflux temperature of 160°C. The stoichiometry was such that 0-10% excess of 4,4′-difluorobenzophenone was present to control molecular weight. A temperature of 160°C was maintained until all of the water of reaction had been collected (3-4 hours). Additional 4,4′-difluorobenzophenone in NMP was then added to ensure endcapping with fluorine. The reaction was continued for 1 hour after which toluene was removed quantitatively from the reaction flask by following the volume of toluene removed from the dean stark trap. The

reaction mixture was then cooled to room temperature and the polymer precipitated in methanol, washed with methanol and water, then dried under vacuum. The purified oligomer was then analyzed for fluorine (appendix F) to obtain an estimate of the number average molecular weight. In the second step, the oligomeric BPAPK and a stoichiometric amount of 4-aminophenol were placed into a 4 neck flask equipped as above. Toluene and NMP were added via cannula. The ratio of these two solvents is such that a stable reflux temperature of 135°C is obtained (NMP/toluene = 1/1). It is important to keep the temperature as low as possible to prevent significant attack by the amine group(34). When the reaction mixture reaches 100°C, a stoichiometric amount of oxygen-free 50% potassium hydroxide in water is added via cannula. An excess of base must be avoided to prevent attack by the amine at the fluorine end groups and/or attack at the carbonyls(35). A temperature of 135°C is maintained until all of the water of reaction has been collected (1.5-2 hrs). Again toluene is removed quantitatively from the reaction mixture. The amine-terminated oligomer is then precipitated in distilled water, washed with water and dried. Elemental analysis for fluorine is again carried out to estimate the amine termination efficiency. A non-aqueous amine titration is also performed to confirm the amine termination efficiency (appendix F).

2.2.2 Resin Formulation

The functionalised oligomers were slowly added to the epoxy resins at 120-150°C while mixing vigorously. A prereaction period of 1/2 hour was allowed followed by the addition of DDS or MDA. Mixing was continued for 5 minutes. At this point, upon cooling, the resin is in a B-stage. All formulations reported had sufficient tack and drape in this B-stage at room temperature for conventional prepreg lay up procedures. These formulations were made at amine to epoxide rations of 1.20 or 1.00 as indicated. The DDS containing reaction mixtures were then degassed under vacuum at 180°C for 3 to 5 minutes and transferred to preheated aluminum sheet molds also at 180°C. These resins were then cured for 2 hours at 180°C followed by 2 hours at 200°C under vacuum. The MDA containing reaction mixtures were degassed at 150°C for 3 to 5 minutes followed by transfer to preheated aluminum sheet molds also at 150°C. These resins were cured for 1 hour at 150°C, 2 hours at 180°C followed by 2 hours at 200°C under vacuum. The sheets were then allowed to cool slowly to room temperature to minimize thermal stresses. Compact tension and three point bend samples were cut from these sheets using a jewelers slotting blade on a Bridgeport milling machine (appendix A). Precracks were inserted by an above Tg insertion technique(36).

2.2.3 Mechanical Property Characterization

Critical stress intensity factors (K_{Ic}) and fracture energy (G_{Ic}) determinations were made on compact tension samples following a modified ASTM E399-83 procedure(37-39)(appendix B). The fracture data reported may not be true K_{Ic} and G_{Ic} values as a result of the thin compact tension samples used and the uncertainty of the satisfaction of the plain strain condition assumed in the derivation of the ASTM E399 equations. Due to the very small amounts of material available for testing, an investigation into the effect of thickness could not be carried out. The fracture surfaces did not suggest plane stress conditions nor was their significant plastic deformation prior to the initiation of crack growth since $P_{max}/P_Q \leq 1.0$. P_{max} and P_Q are as defined in ASTM E399.

Young's modulus calculations were performed in three point bend following ASTM D790M (appendix C). Both determinations were carried out on an Instron testing machine at a crosshead speed of .05cm/minute. Dynamic mechanical measurements were made on an IMASS Dynastat in three point bend (appendix D). Differential scanning calorimeter (DSC) measurements were made using a Perkin Elmer DSC II. Solvent resistance behavior was measured in terms of percent absorption by weight of water, methylene

chloride, methyl ethyl ketone, jet fuel, deicing fluid, and hydraulic fluid (appendix E).

2.3 Results and Discussion

An aromatic amine terminated BPAPK having a number average molecular weight of 4,400 and an amine termination efficiency of greater than 85% was synthesized and incorporated into three different epoxy resins at various weight percentages. Figure 2.2 is a DSC scan of this 4,400 Mn BPAPK prior to amine termination. This scan shows a glass transition temperature of approximately 115°C. The three resins investigated were Epon 828, Heloxy 69 and MY 720, the diglycidyl ethers of bisphenol A and resorcinol, and the tetraglycidyl ether of methylene dianiline respectively. Table 2.1 summarizes the mechanical properties of these cured matrices. For standard deviation data see appendix G. Phase separation was visibly evident in all of the cured materials. In Heloxy 69, phase separation was visible on a macroscopic scale, having occurred when the viscosity of the material was still low enough to allow macroscopic aggregation to occur. In the Epon 828 and MY 720 formulations the cured resins were opaque suggesting phase separation into domains having sizes on the order of the wavelength of visible light. In Epon 828 and MY720 phase separation must occur at a point closer

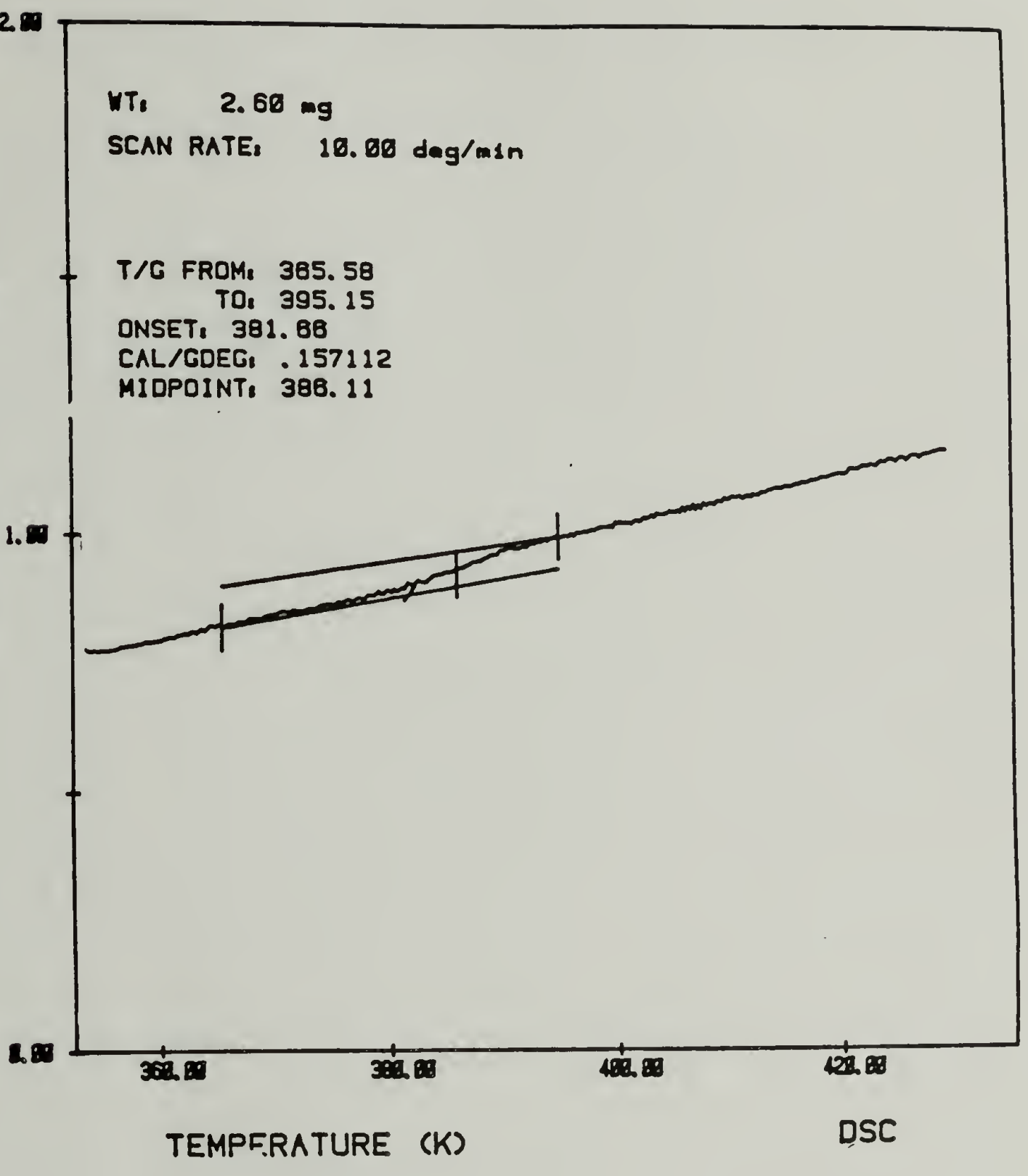


Figure 2.2 Differential Scanning Calorimeter Scan of Bisphenol A Polyetheretherketone.

Table 2.1.

Mechanical Property Data for Resins Formulated Using An Amine Terminated Bisphenol A Polyaryletherketone of Mn = 4,400 and Amine termination Efficiency of > 85%

EPOXY RESIN	% MOD	AMINE	A/E	Tg °C	E GPa	K_{IC} $N/M^{3/2}$	G_{IC} J/M^2	PHASE SEP.
H69	0	DDS	1.2	175	3.01	$.88 \times 10^6$	257	No
H69	20	DDS	1.2	130	3.12	1.2×10^6	409	Macro
H69	35	DDS	1.2	120	3.18	1.5×10^6	682	Macro
H69	40	DDS	1.2	120	3.27	1.5×10^6	712	Macro
E828	0	DDS	1.2	200	2.16	$.89 \times 10^6$	368	No
E828	25	DDS	1.2	155	2.42	$.91 \times 10^6$	343	Micro
E828	35	DDS	1.2	140	2.61	1.1×10^6	499	Micro
E828	40	DDS	1.2	135	2.92	1.2×10^6	520	Micro
MY720	0	DDS	1.2	260	3.08	-------	---	No
MY720	25	DDS	1.2	170* (220)	3.03	1.0×10^6	341	Micro

* Refers to systems having two glass transition temperatures as detected in the dynamic mechanical analysis. The second Tg is listed is parenthesis below the first Tg.

Phase separation type refers to phase morphology. Type A has an epoxy resin/ DDS rich continuous phase with BPAPK rich inclusions. Type B has a BPAPK rich continuous phase with epoxy/ DDS rich inclusions. UK refers to samples not investigated with TEM.

to gelation than the phase separation in the Heloxy 69 formulations. Since phase separation and gelation are thermodynamic and kinetic processes, the Epon 828 and My 720 resins must have a combination of solubility parameter, viscosity behavior and cure kinetics which provide for this small domain size. For composite use, where inter fiber spacing is approximately 3 to 5 microns, the Heloxy 69 formulations would not be suitable as a result of the macroscopic phase separated domains. The small domain sizes in the Epon 828 and MY 720 formulations would be more suited to composite applications. The viscosity of the MY 720 formulations is much higher than that of the Epon 828 formulations making debulking difficult at the higher loading levels. Therefore in subsequent work only Epon 828 was used. All of the formulations investigated had sufficient tack and drape at room temperature for conventional prepreg lay up procedures. The amount of tack and drape decreased with increasing functionalised oligomer weight fraction. In all three epoxy resins it was discovered that K_{Ic}, G_{Ic} and Young's modulus increased with the weight percent amine terminated BPAPK added. Figure 2.3 is a plot of Young's modulus vs. weight concentration of the functionalised oligomer for the Epon 828, Heloxy 69 and My720 formulations. Increases in stiffness of 35%, 9%, and 6% were obtained for the highest loadings respectively. Figure 2.4. is a plot of the critical stress intensity factor vs. weight concentration of the functionalised

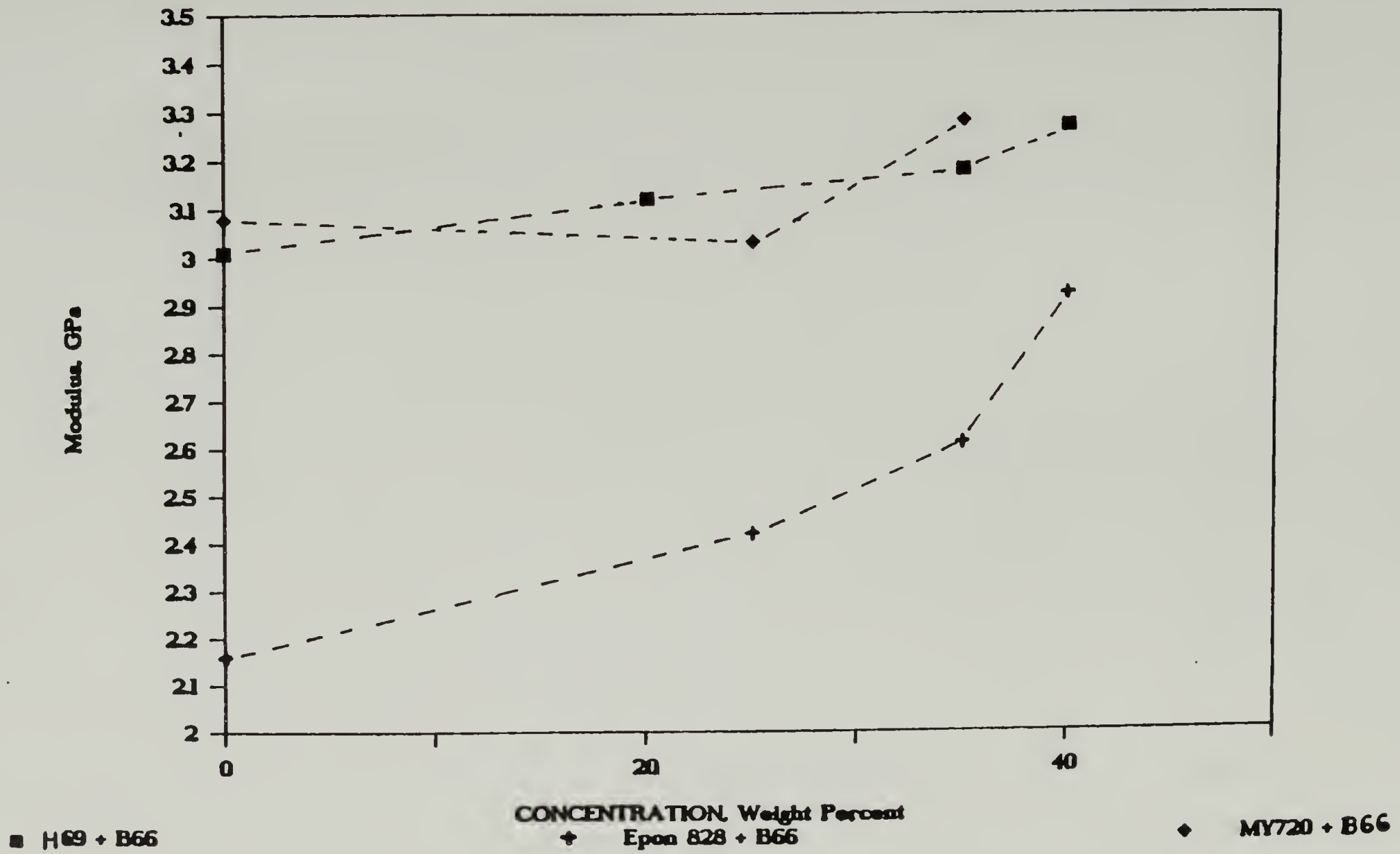


Figure 2.3 Young's Modulus vs. Concentration of 4,400 Mn BPAPK in Epon 828, Heloxy 69, and MY 720.

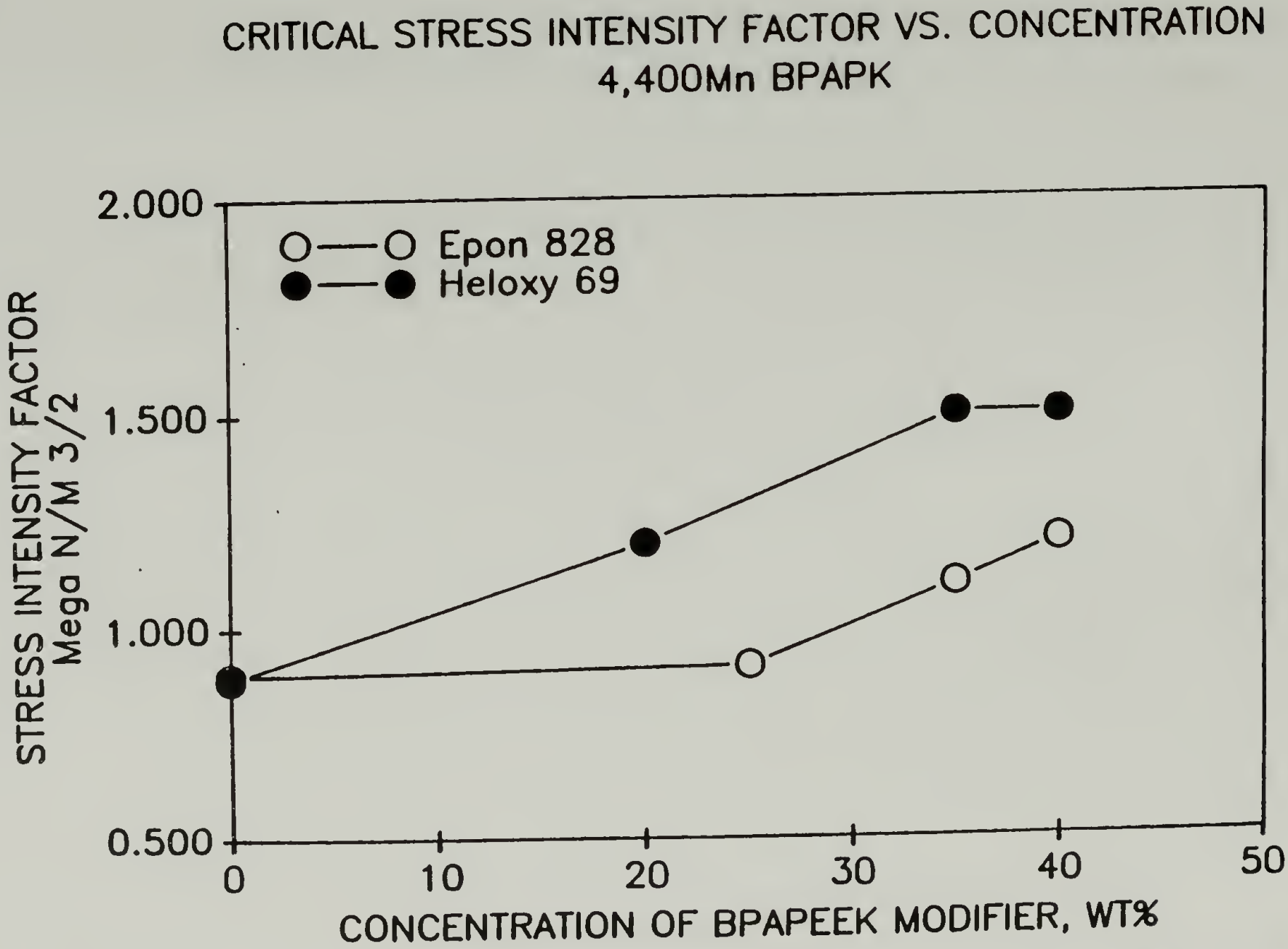


Figure 2.4 Critical Stress Intensity Factor vs. Concentration of 4,400 Mn BPAPK in Epon 828 and Heloxy 69.

oligomer for the Heloxy 69 and Epon 828 formulations. Increases in the K_{Ic} value of 77% and 40% were obtained respectively for the highest loadings in these resins. Figure 2.5 is a plot of the fracture energy (G_{Ic}) versus the weight concentration of 4,400 Mn BPAPK in Epon 828 and Heloxy 69. Figures 2.6.-2.16. are plots of the dynamic storage and loss moduli and loss tangent vs. temperature for the cured resin formulations. Figures 2.6.-2.9. represent the Heloxy 69/DDS/4,400 Mn BPAPK systems at 0, 20, 35, and 40 percent by weight 4,400 Mn BPAPK respectively. Figures 2.10.-2.13. represent the Epon 828/DDS/4,400 Mn BPAPK systems at 0, 25, 35, and 40 percent by weight 4,400 Mn BPAPK respectively. Figures 2.14.-2.16 represent the MY 720/DDS/4,400 Mn BPAPK systems at 0, 25, and 35 percent by weight 4,400 Mn BPAPK. Despite the phase separation which occurred in each of these formulations, only one glass transition is seen in most of the dynamic mechanical spectra of the cured modified resins. Since the BPAPK modifier is at a low molecular weight, incomplete phase separation must have occurred in the Heloxy 69 and Epon 828 resins leading to the presence of significant amounts of the BPAPK in both phases. In this situation the glass transition temperatures of the two phases would be expected to be close, and therefore indistinguishable. In the MY720 formulations two glass transition temperatures were observed. Phase separation in this resin occurred to a sufficient extent such that two distinguishable glass transition temperatures

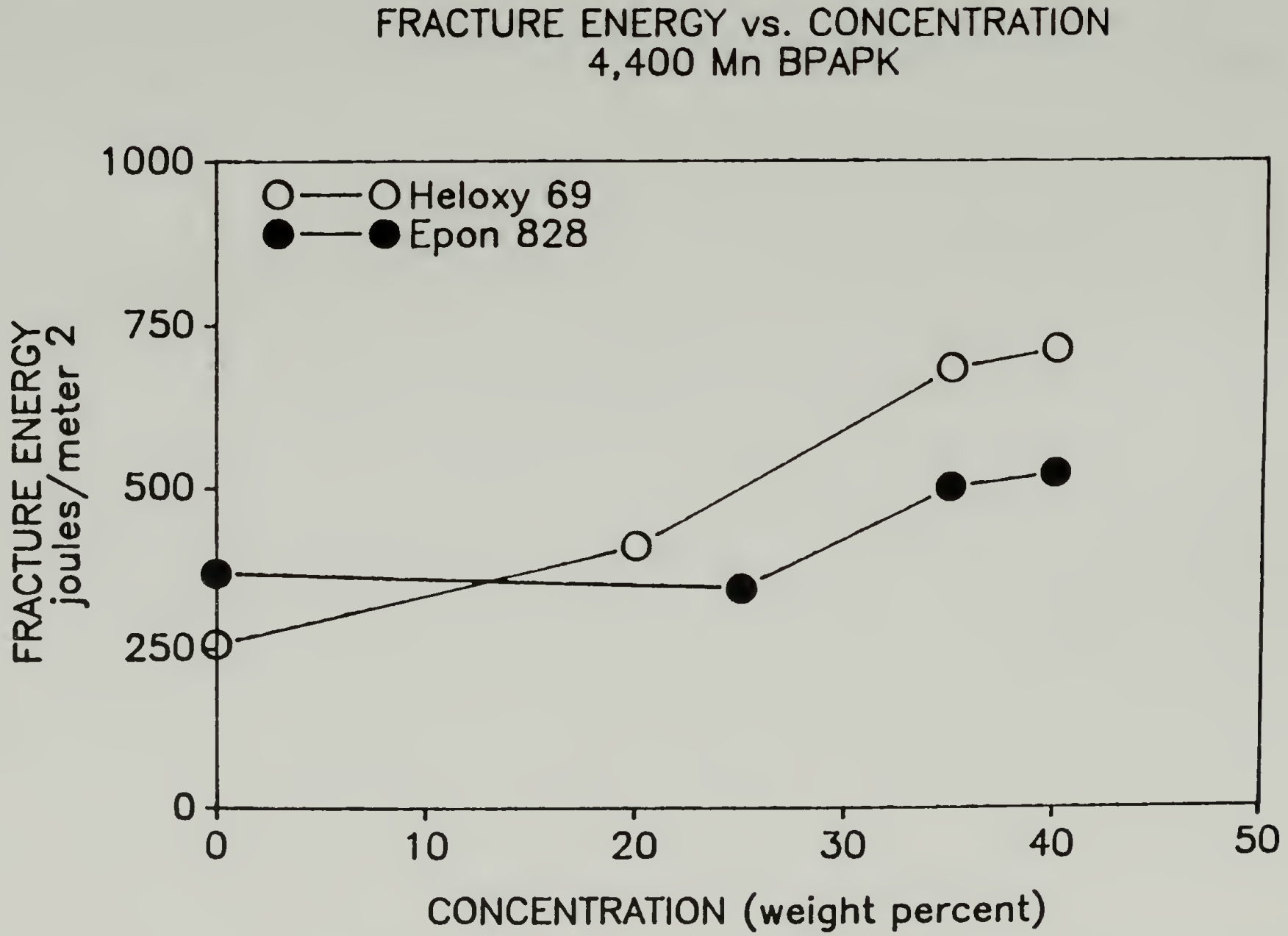


Figure 2.5 Fracture Energy vs. Concentration of 4,400 Mn BPAPK in Epon 828 and Heloxy 69.

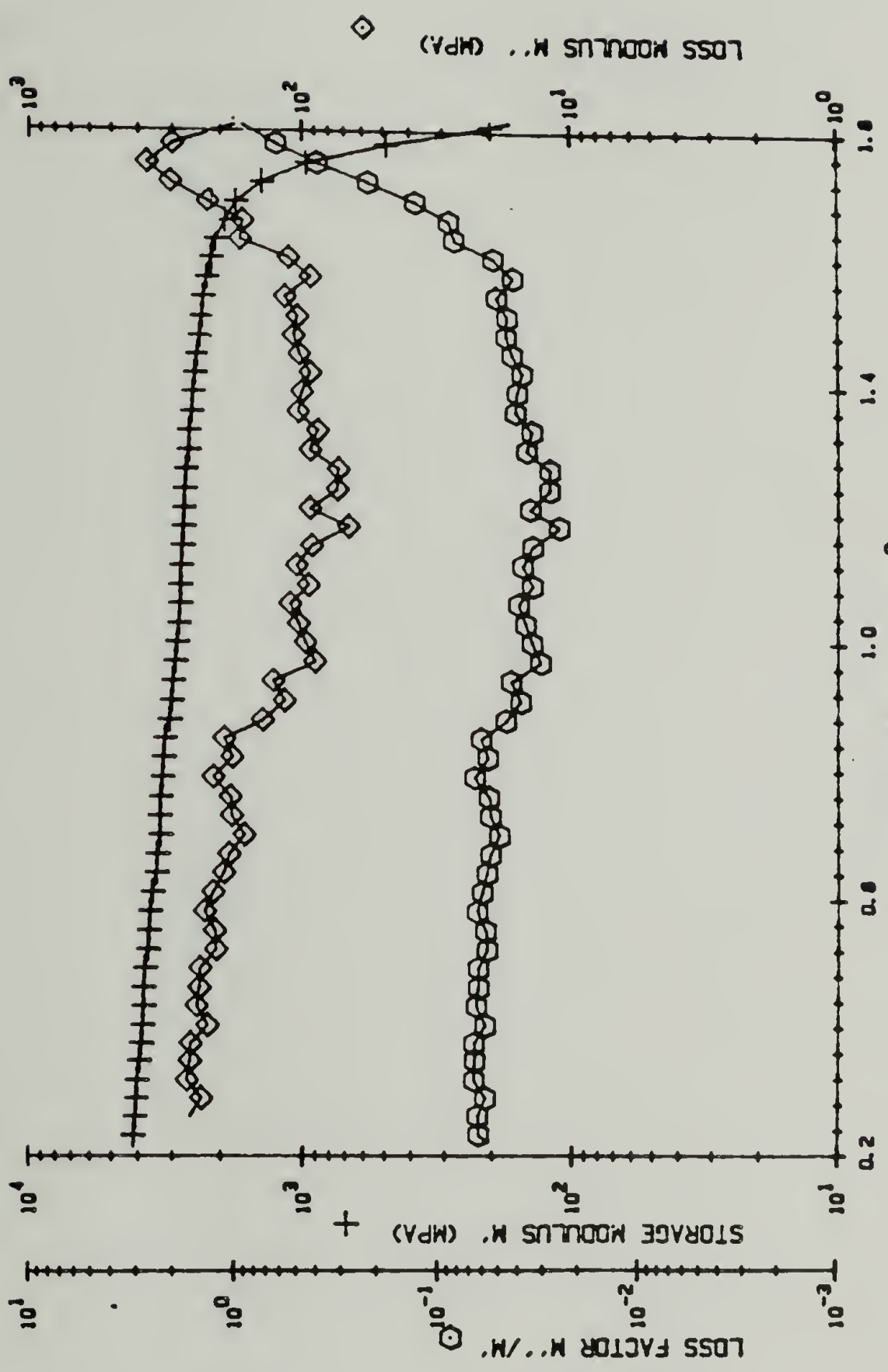


Figure 2.6 Dynamic Mechanical Properties of Heloxy 69/ DDS/ A/E = 1.2.

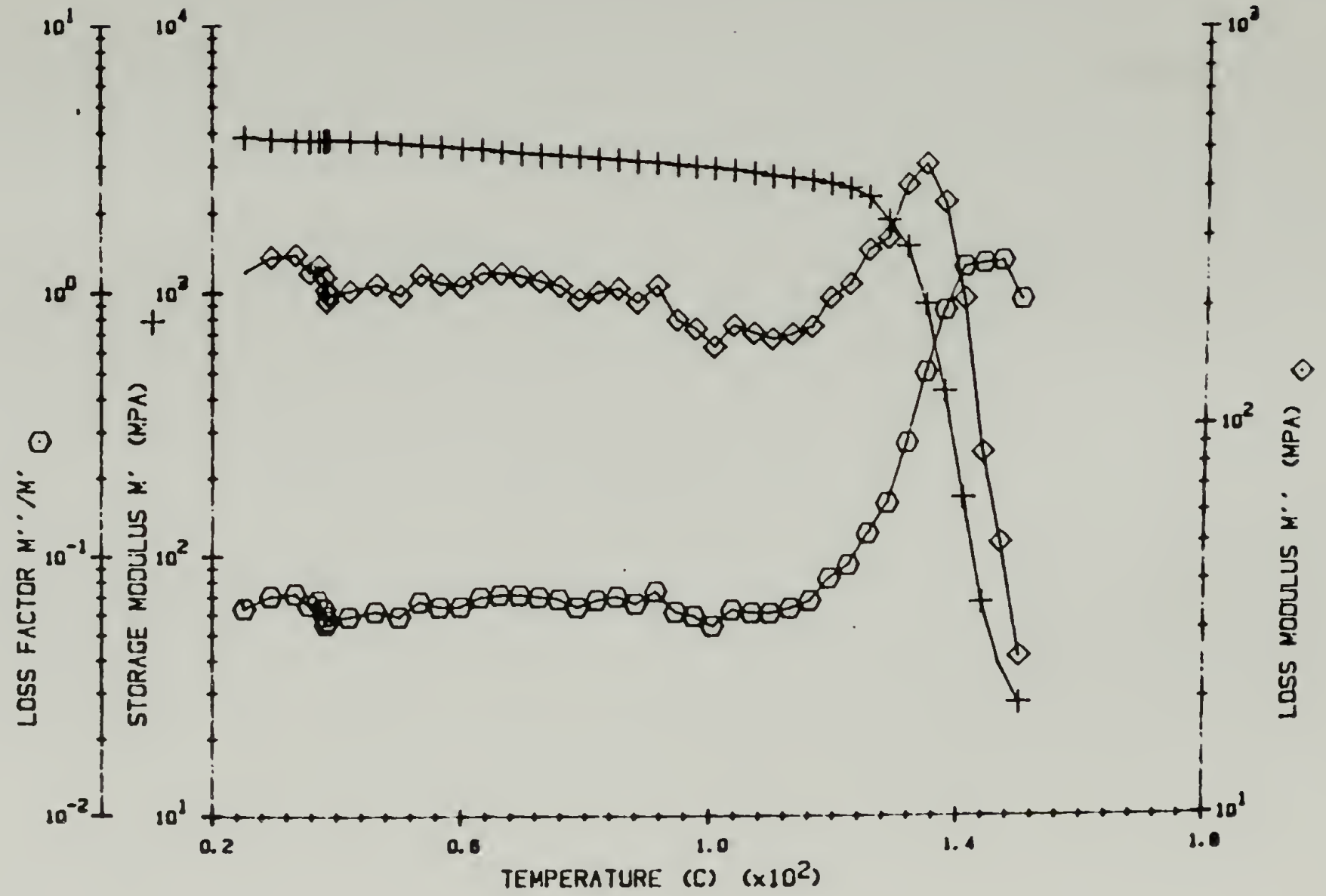


Figure 2.7 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 20% 4,400 Mn BPAPK/ A/E = 1.2.

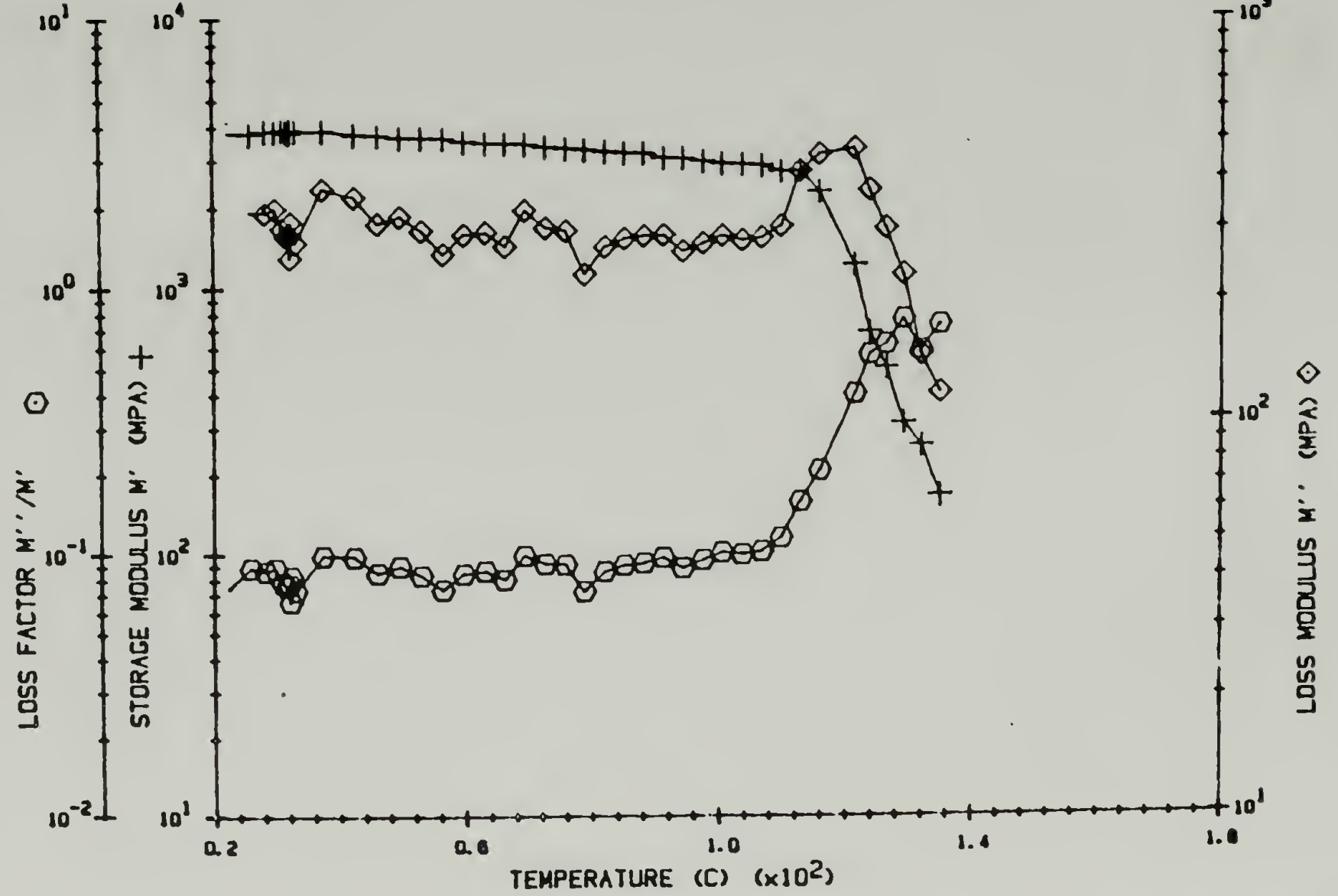


Figure 2.8 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 35% 4,400 Mn BPAPK/ A/E = 1.2 .

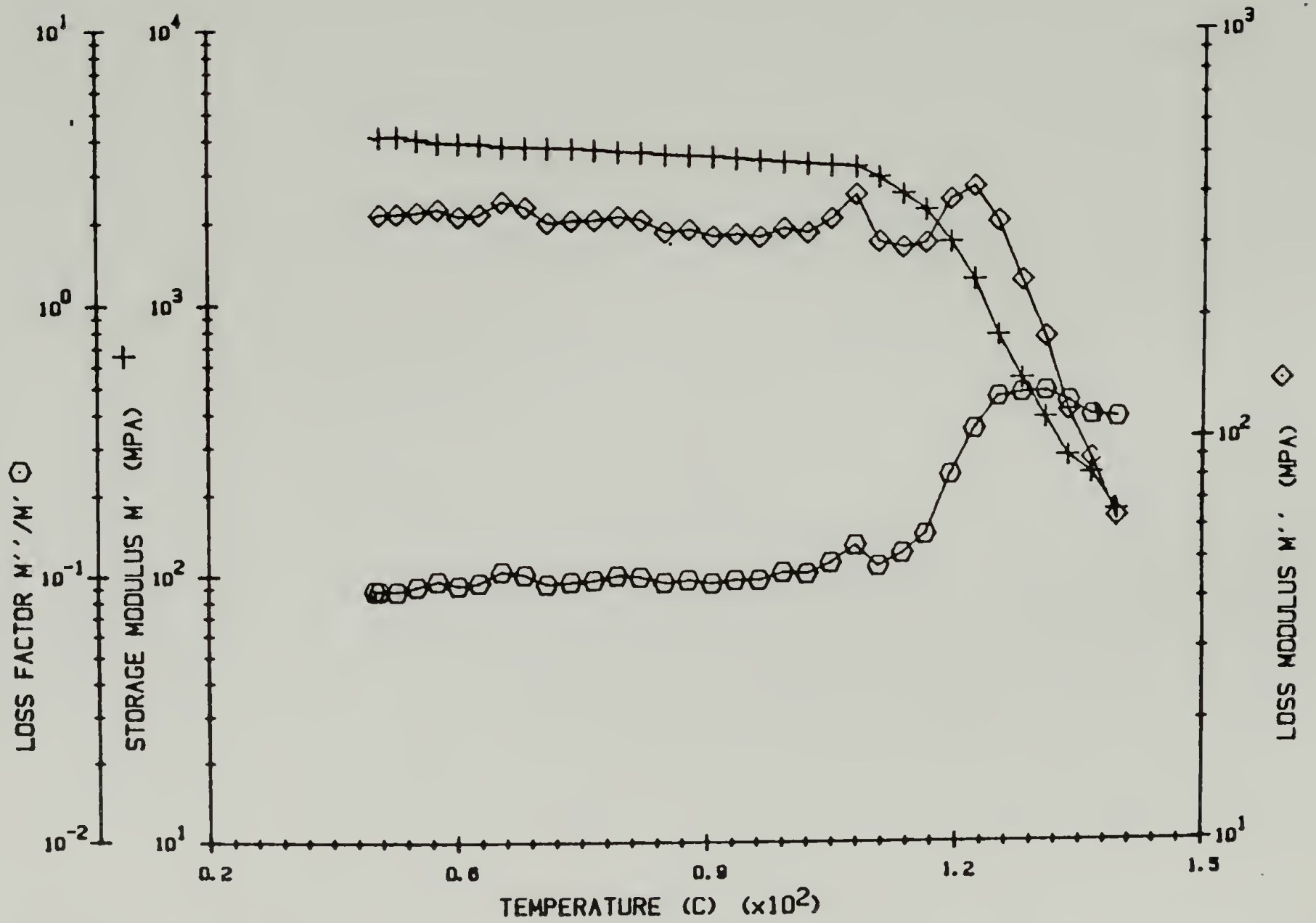


Figure 2.9 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 40% 4,400 Mn BPAPK/ A/E = 1.2.

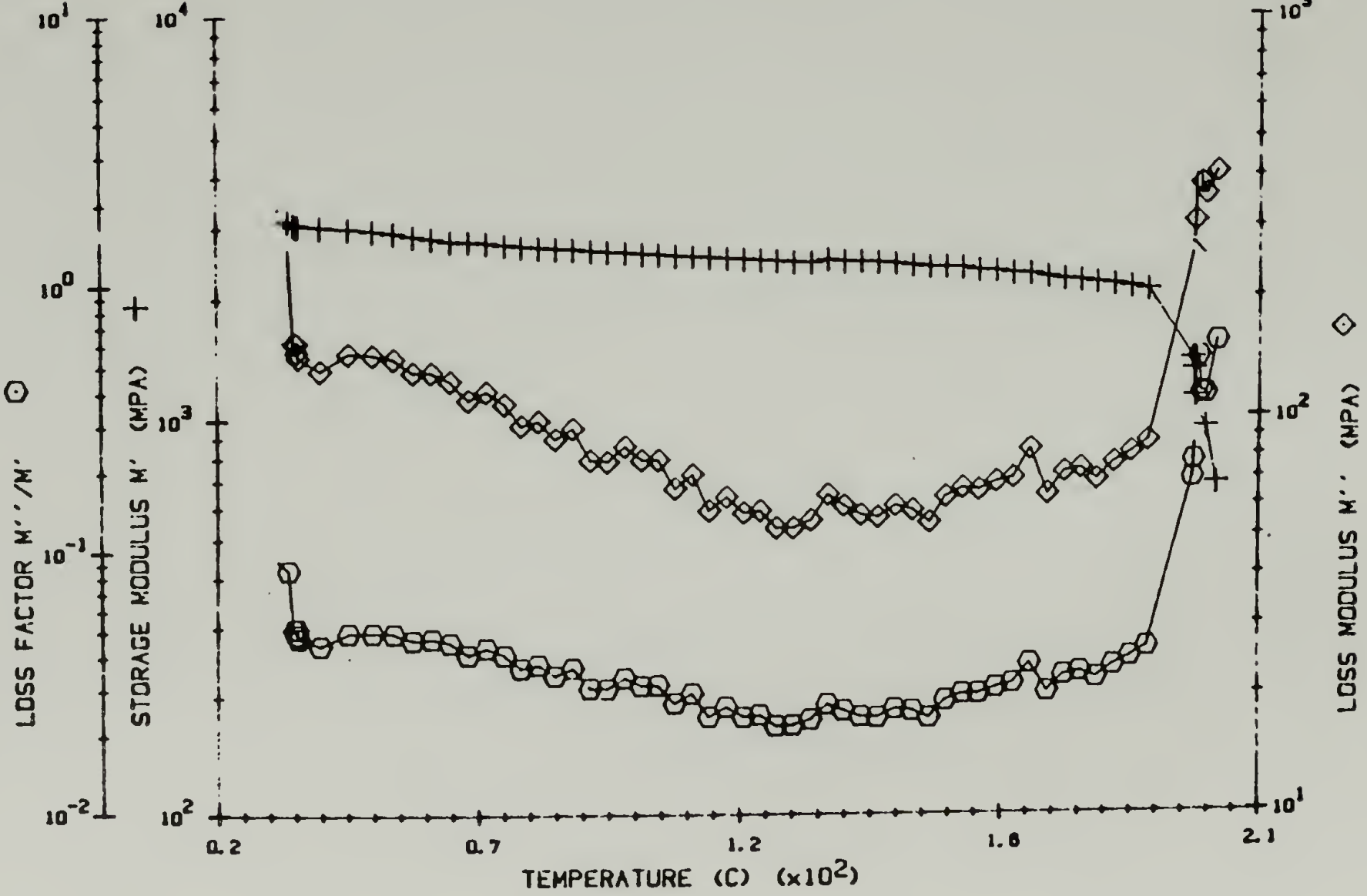


Figure 2.10 Dynamic Mechanical Properties of Epon 828/ DDS/ A/E = 1.2.

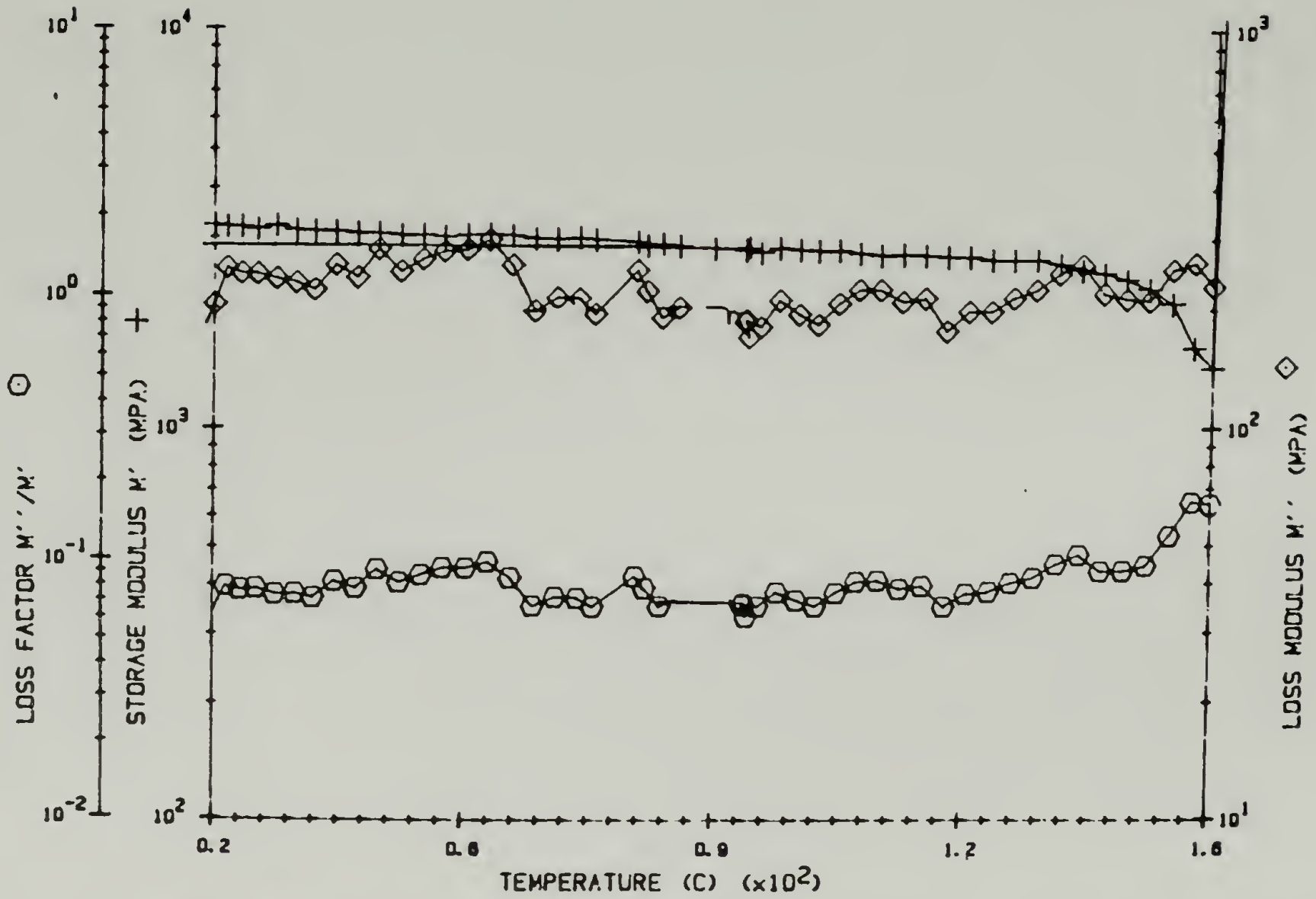


Figure 2.11 Dynamic Mechanical Properties of Epon 828/ DDS 25% 4,400 Mn BPAPK/ A/E = 1.2.

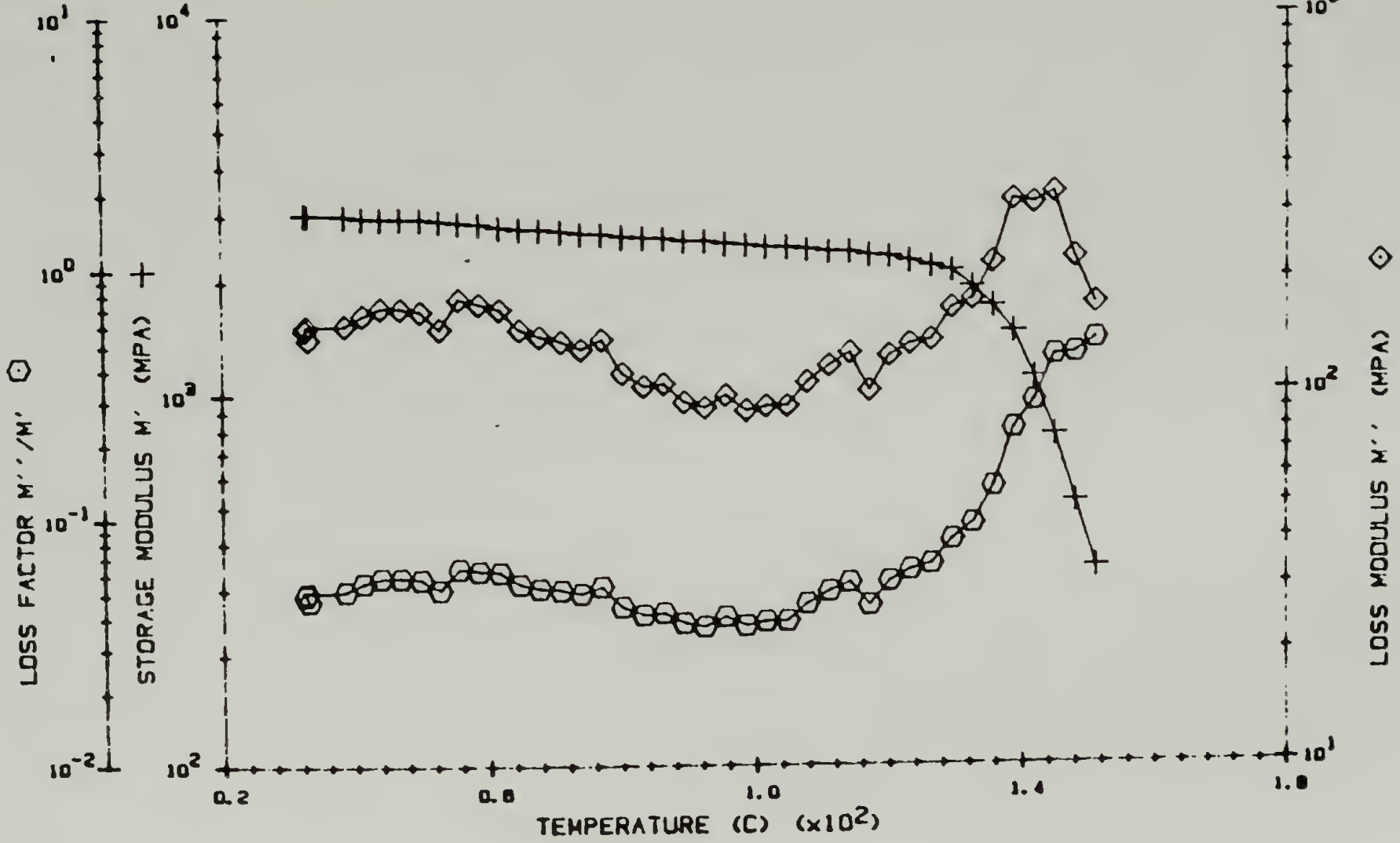


Figure 2.12 Dynamic Mechanical Properties of Epon 828/ DDS/ 35% 4,400 Mn BPAPK/ A/E = 1.2.

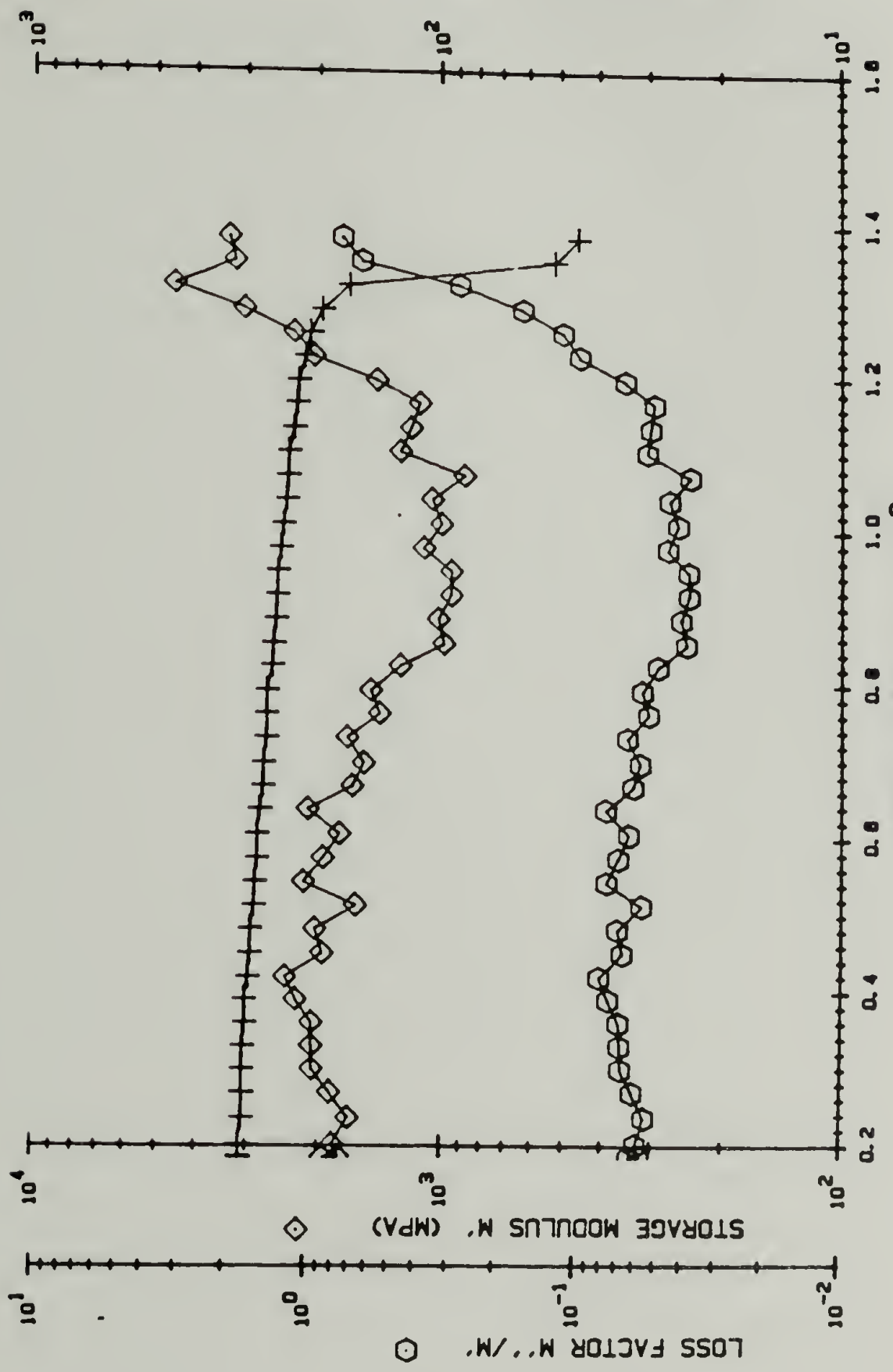


Figure 2.13 Dynamic Mechanical Properties of Epon 828/ DDS/ 40% 4,400 Mn BPAPK/ A/E = 1.2.

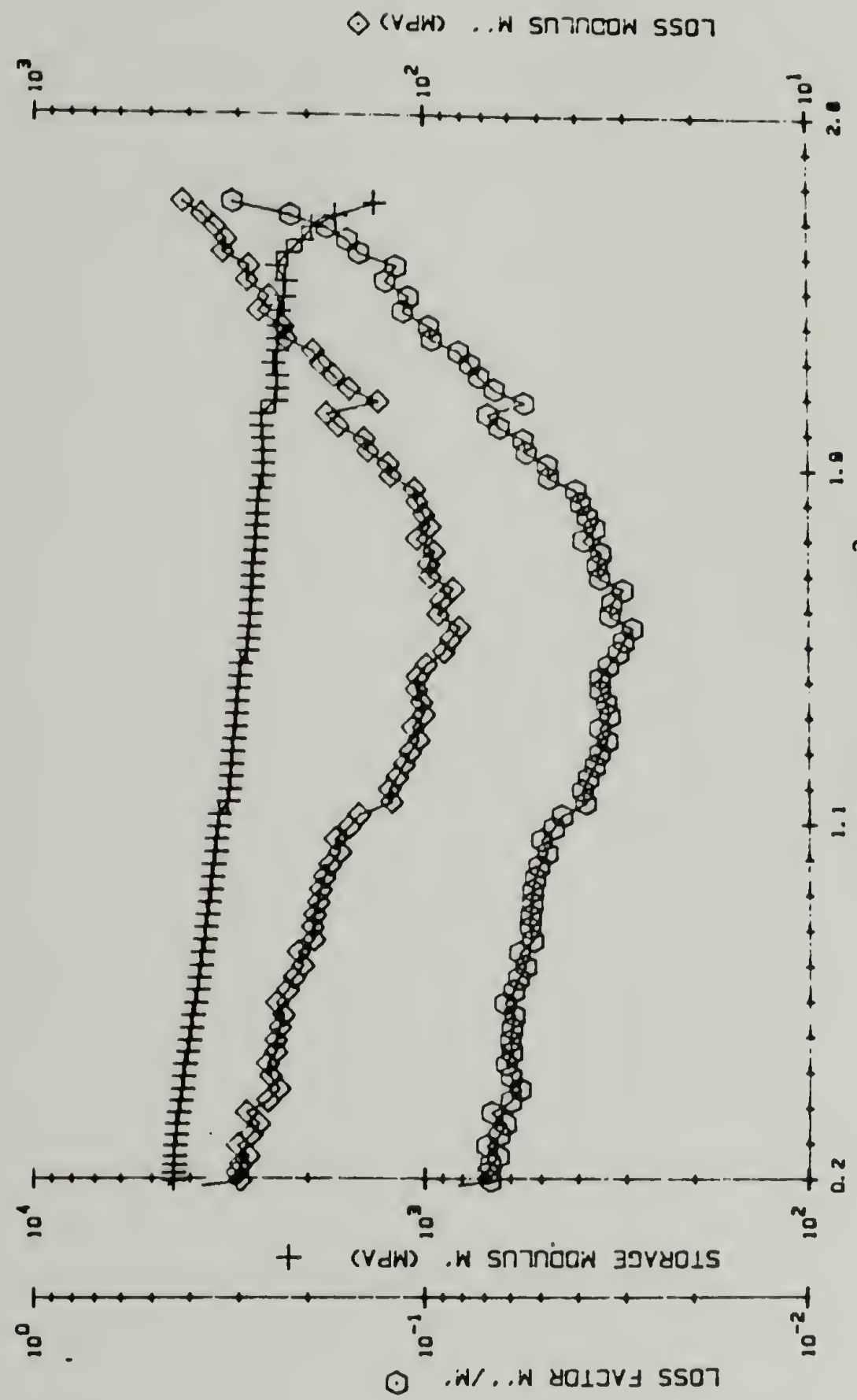


Figure 2.14 Dynamic Mechanical Properties of MY720/ DDS/ A/E = 1.2.

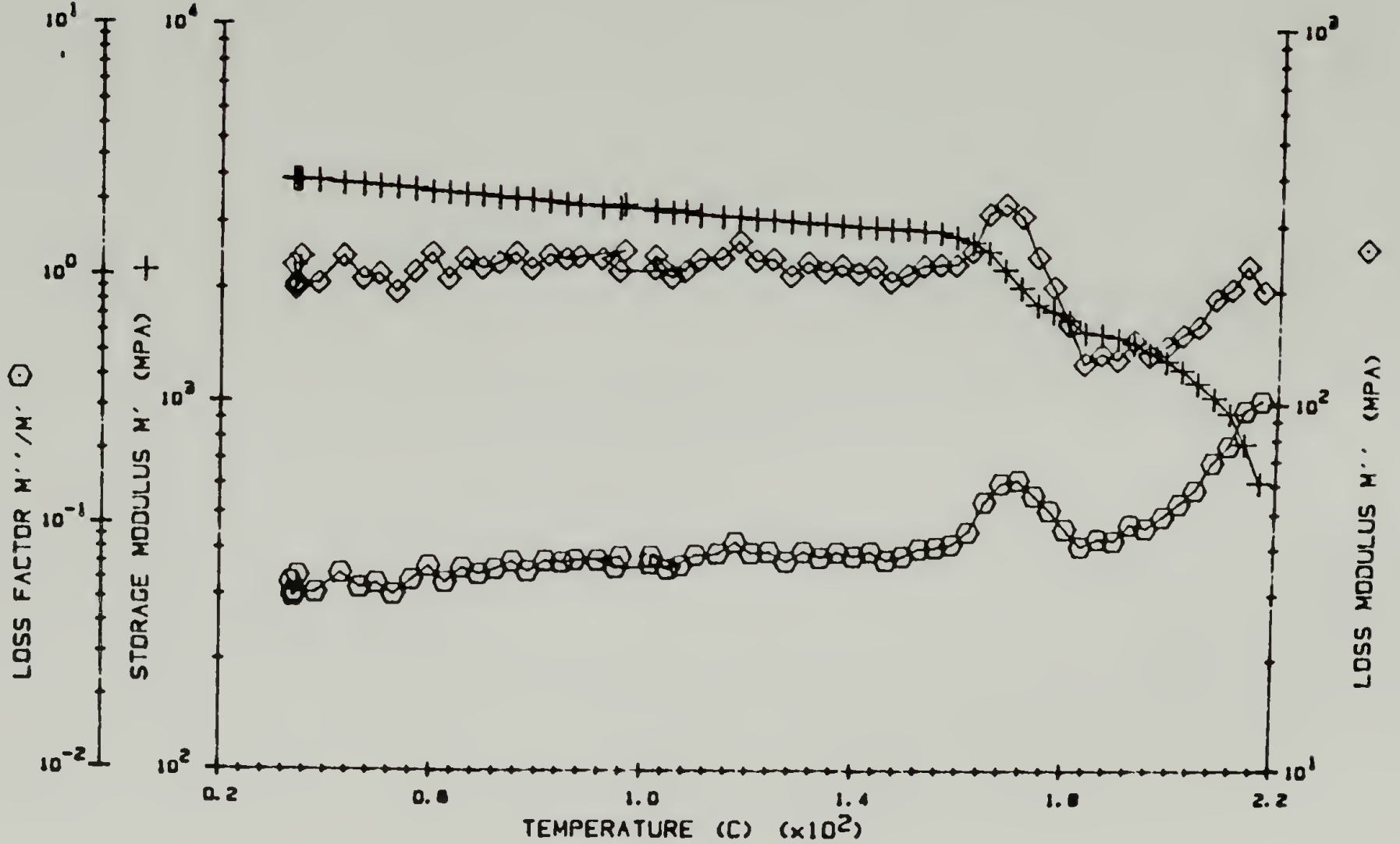


Figure 2.15 Dynamic Mechanical Properties of MY720/ DDS/ 25% 4,400 Mn BPAPK/ A/E = 1.2.

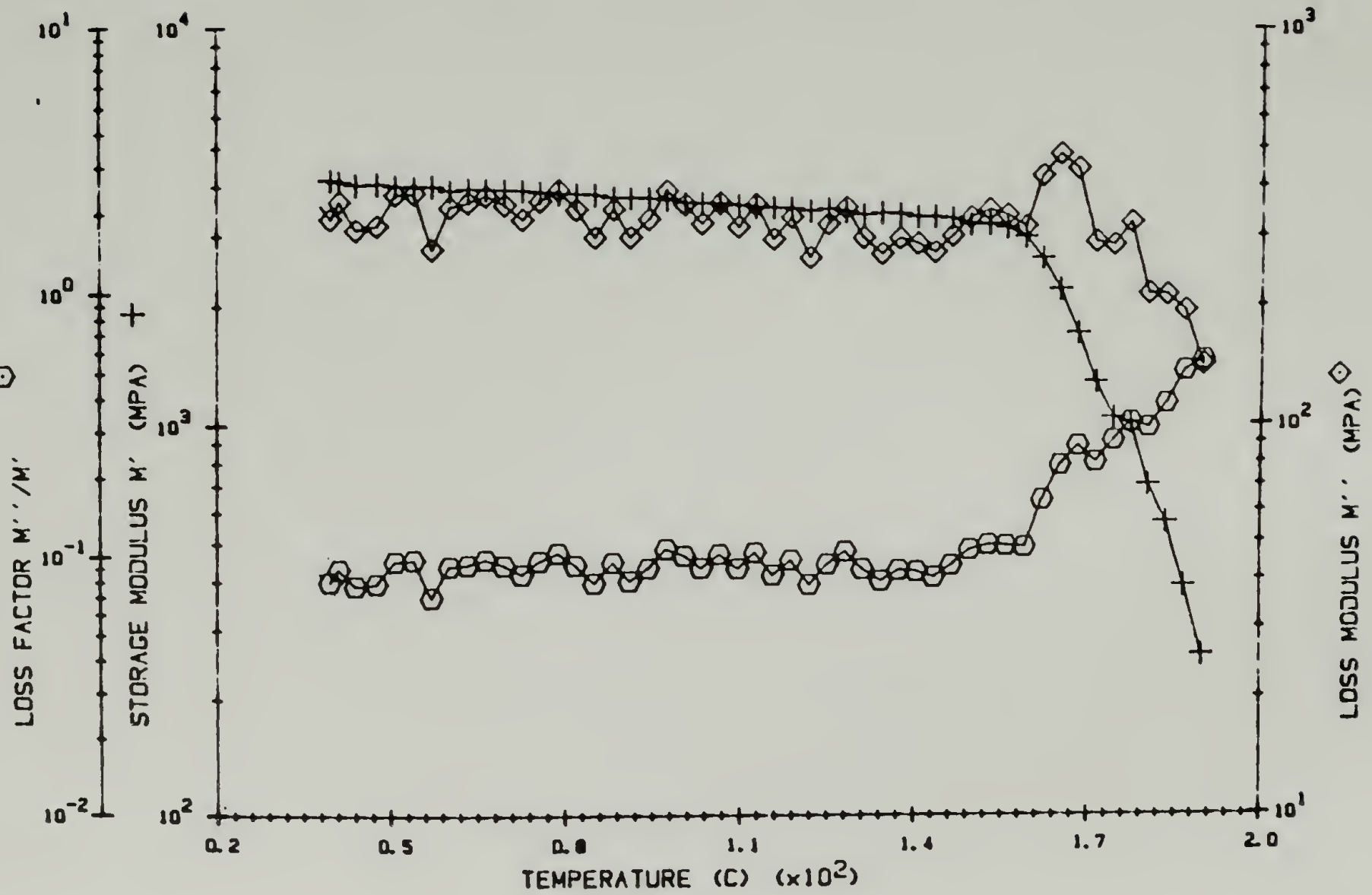


Figure 2.16 Dynamic Mechanical Properties of MY720/ DDS/ 35% 4,400 Mn BPAPK/ A/E = 1.2.

could be measured. The fact that neither Tg equals that of the neat resin suggests that phase separation was not complete. From the dynamic mechanical data it was observed that the glass transition temperature decreased with increasing weight percent functionalised oligomer in the three epoxy resin systems investigated. The glass transition temperature was taken as the point at which the dynamic loss modulus reached a peak value. The glass transition temperature was as low as 120°C in the formulations with the highest levels of functionalised oligomer. The glass transition temperatures, K_{Ic}, G_{Ic}, and Young's moduli for these 4,400 Mn BPAPK resin formulations are tabulated in Table 2.1. For standard deviation data see appendix G.

In Table 2.2, data on two higher molecular weight BPAPKS in Epon 828 is tabulated. For standard deviation data see appendix G. These formulations, using a 7,000 Mn BPAPK and a 21,000 Mn BPAPK, were made at an amine to epoxide ratio of 1.0 to achieve a glass transition temperature above that of the formulations in Table 2.1. The methylenedianiline/Epon 828 system was used for the 21,000 Mn BPAPK as a result of the incompatibility of this high molecular weight polymer with the diamino diphenyl sulphone/Epon 828 system. In both cases large increases in K_{Ic} and G_{rc} over the neat resins are obtained. For the 40% loading of the 7,000 number average molecular weight BPAPK a G_{Ic} value of 2,400 J/M^2 is obtained. This value represents

Table 2.2.

Mechanical Property Data for Formulations Using Two Higher Molecular Weight Amine Terminated Bisphenol A Polyaryletherketones of Mn = 7,000 and 21,000 having amine termination efficiencies of >83% and >80% respectively.

EPOXY RESIN	% MOD	AMINE	A/E	Tg °C	E GPa	K_{Ic} $N/M^{3/2}$	G_{Ic} J/M^2	PHASE SEP.	TYPE SEP.
7,000 Mn BPAPK									
E828	0	DDS	1.0	210	2.52	$.89x10^6$	315	No	
E828	20	DDS	1.0	145* (200)	2.55	$1.6x10^6$	905	Micro	A
E828	30	DDS	1.0	145	2.47	$1.8x10^6$	1388	Micro	B
E828	40	DDS	1.0	145	2.49	$2.5x10^6$	2344	Micro	B
21,000 Mn BPAPK									
E828	0	MDA	1.0	185	2.33	$.81x10^6$	281	No	
E828	10	MDA	1.0	175	2.44	$1.1x10^6$	517	Micro	A
E828	20	MDA	1.0	160* (185)	2.36	$1.5x10^6$	893	Micro	UK
E828	25	MDA	1.0	160	2.42	$1.8x10^6$	1350	Micro	B

* Refers to systems having two glass transition temperatures as detected in the dynamic mechanical analysis. The second Tg is listed in parenthesis below the first Tg.

an increase of 8 fold over the neat resin and approaches that reported for the bisphenol A PEEK thermoplastic material (29). The glass transition temperature levels off at 145°C for these 7,000 Mn BPAPK/Epon 828/DDS systems. In the 21,000 Mn BPAPK/Epon 828/MDA system at a 25% loading level a G_{Ic} value of 1,350 is obtained, an increase of four fold over that of the neat resin. In this system a glass transition temperature of 160°C is maintained.

In Figure 2.17, K_{Ic} vs. the weight concentration of the functionalised oligomer is plotted for the 4,400 Mn, 7,000 Mn, and 21,000 Mn BPAPK systems. The formulations made with the 4,400 Mn oligomer were made at an amine to epoxide ratio of 1.20 while those with the 7,000 and 21,000 Mn oligomers were made at amine to epoxide ratios of 1.0 to achieve higher glass transition temperatures. The K_{Ic} value is again a strong function of the weight percent functionalised oligomer added as well as the number average molecular weight of the functionalised oligomer. In Figure 2.18 G_{Ic} is plotted versus weight concentration of oligomer added for the 4,400 Mn, 7,000 Mn, and 21,000 Mn BPAPK in Epon 828. Young's modulus for these higher molecular weight oligomer formulations is independent of the concentration of the weight percent of the oligomer added.

In Figures 2.19-2.24 load vs. deflection graphs for three point bend beam samples of the Epon 828/ DDS/ 7,000 Mn BPAPK and Epon 828/ MDA/ 21,000 Mn BPAPK samples are shown.

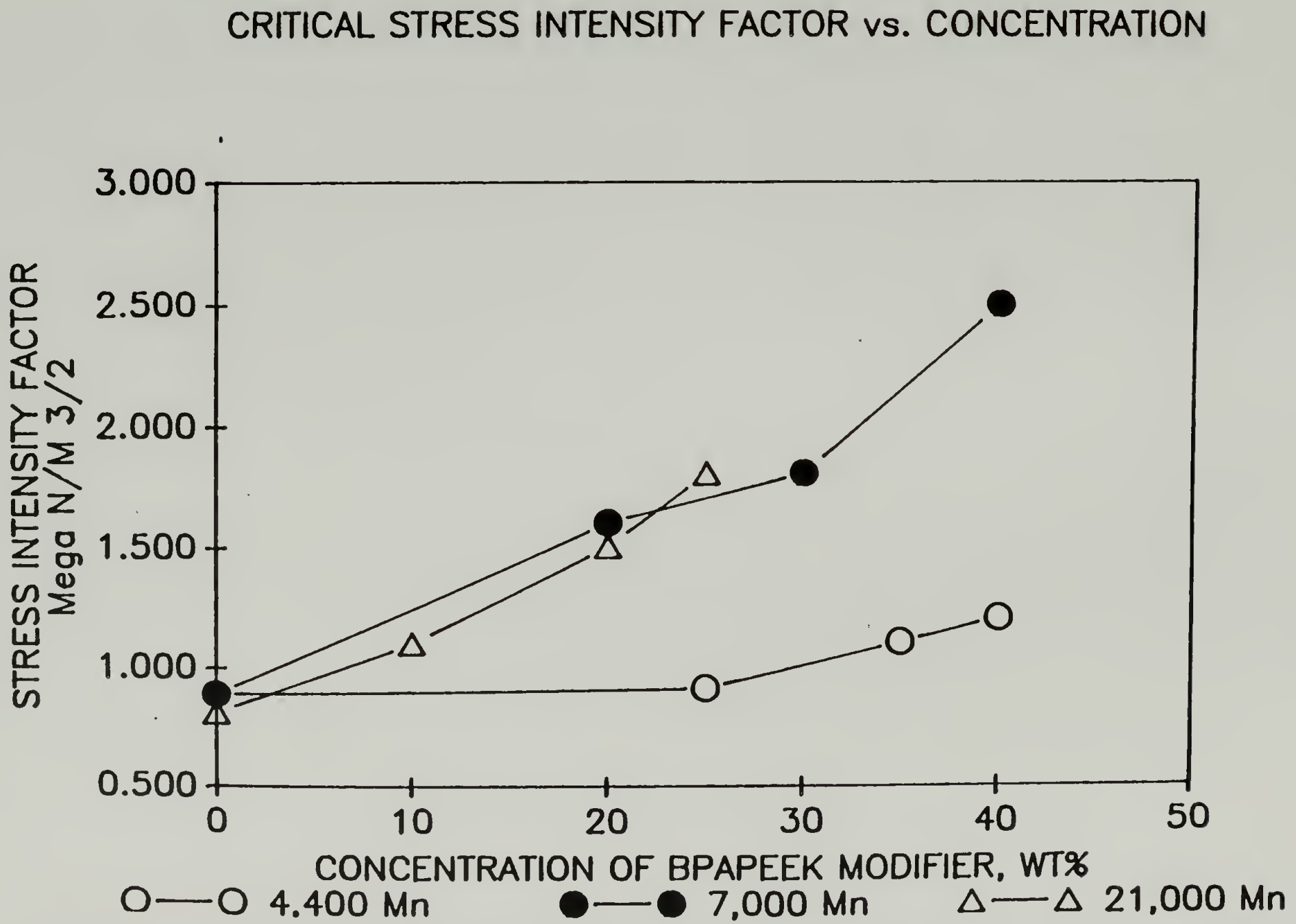


Figure 2.17 Critical Stress Intensity Factor vs. Concentration for the 4,400 Mn, 7,000 Mn, and the 21,000 Mn BPAPKs in Epon 828.

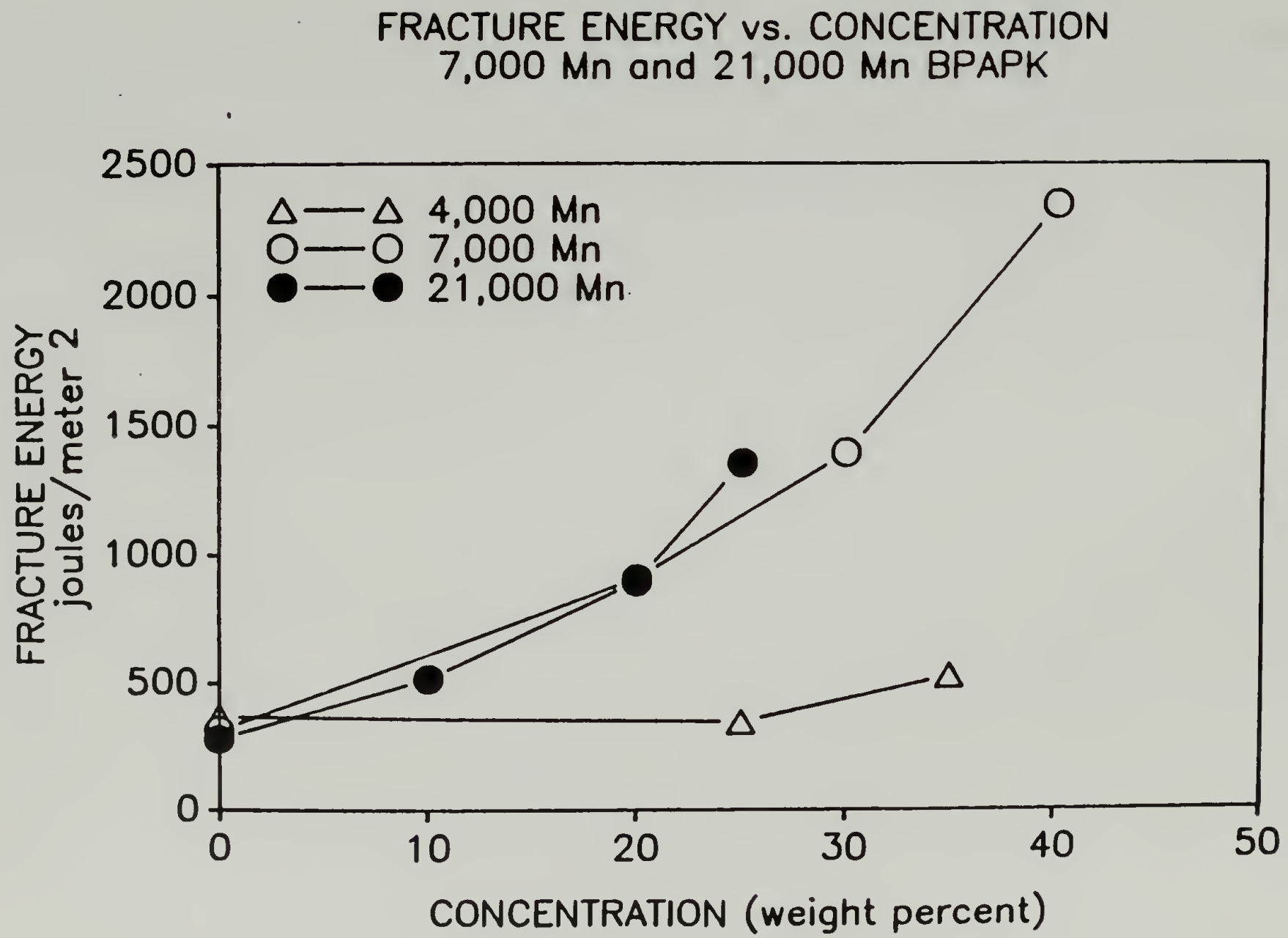


Figure 2.18 Fracture Energy vs. Concentration for the 4,400 Mn, 7,000 Mn, and 21,000 Mn BPAPKs in Epon 828.

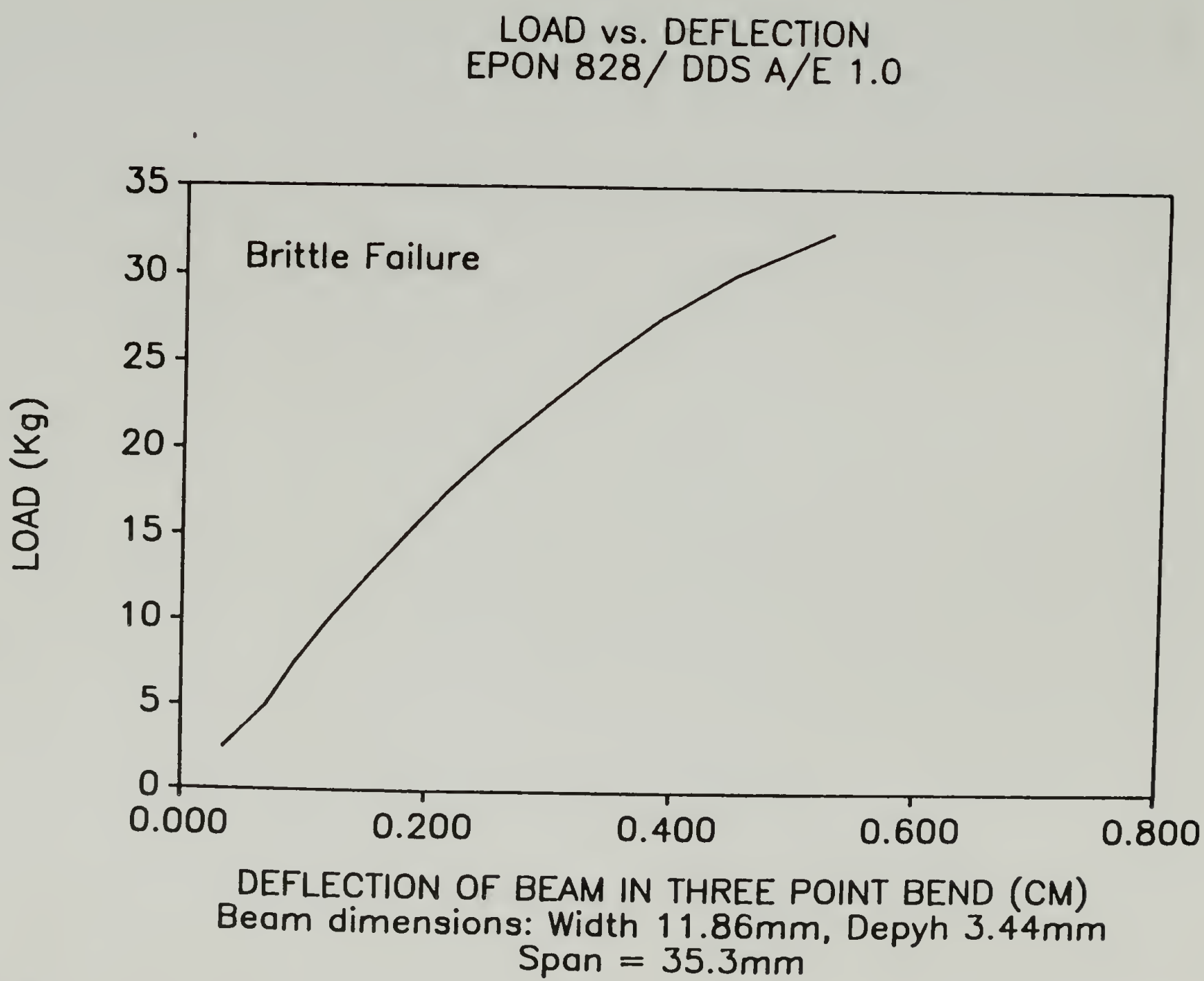


Figure 2.19 Load vs. Deflection of a three point bend beam of Epon 828/ DDS/ A/E = 1.0.

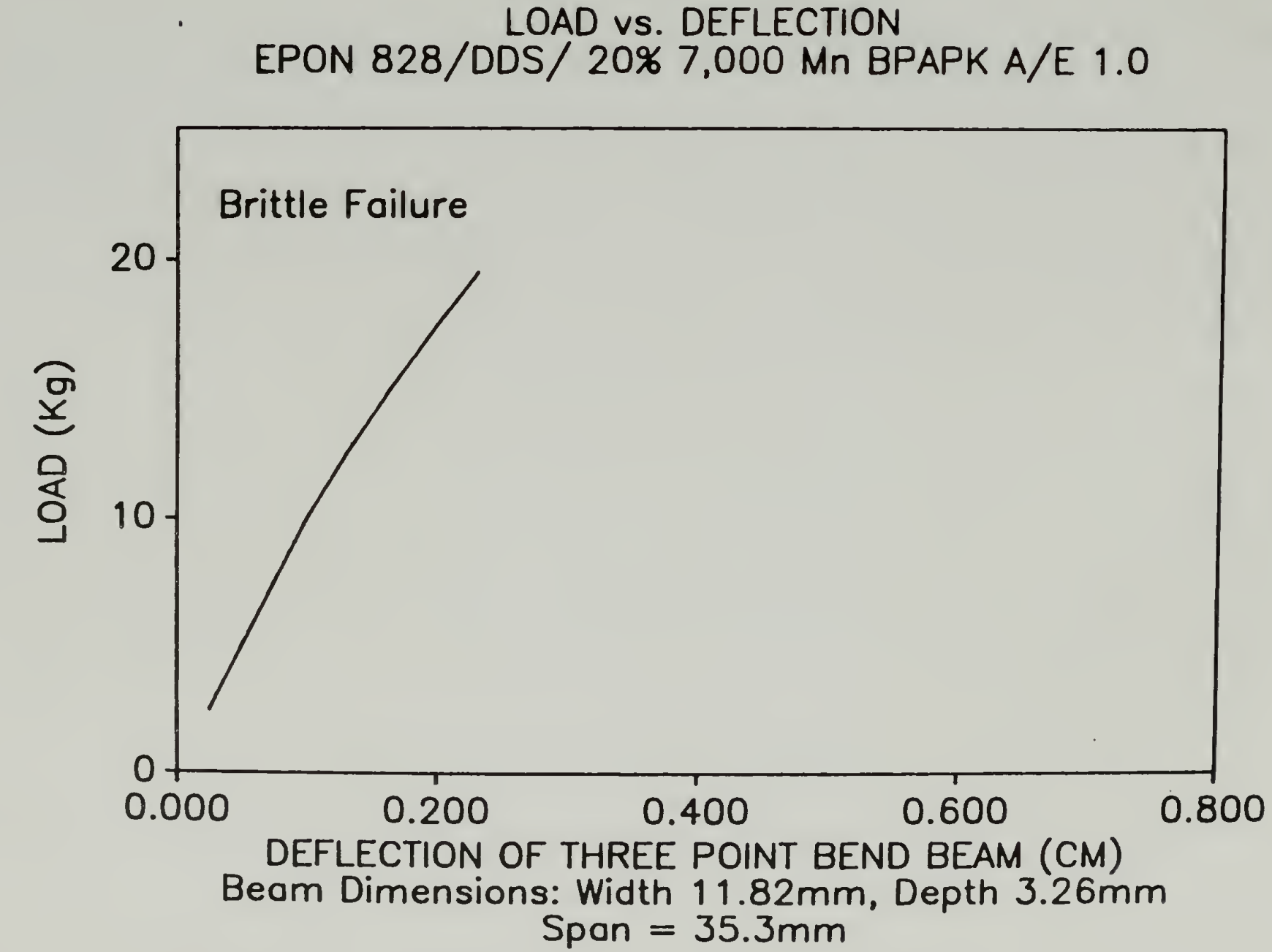


Figure 2.20 Load vs. Deflection of a three point bend beam of Epon 828/ DDS/ 20% 7,000 Mn BPAPK/ A/E = 1.0.

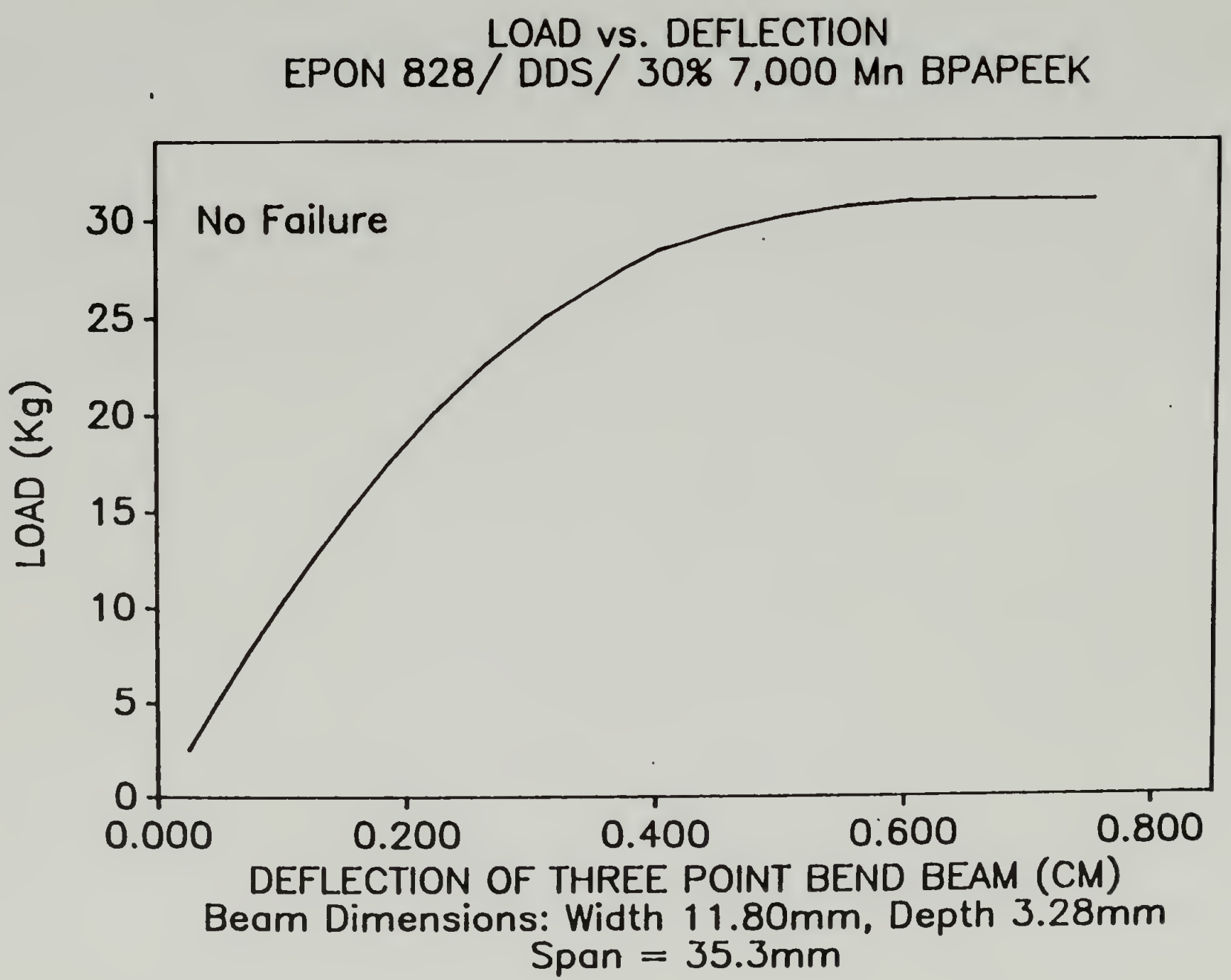


Figure 2.21 Load vs. Deflection of a three point bend beam of Epon 828/ DDS/ 30% 7,000 Mn BPAPK/ A/E = 1.0.

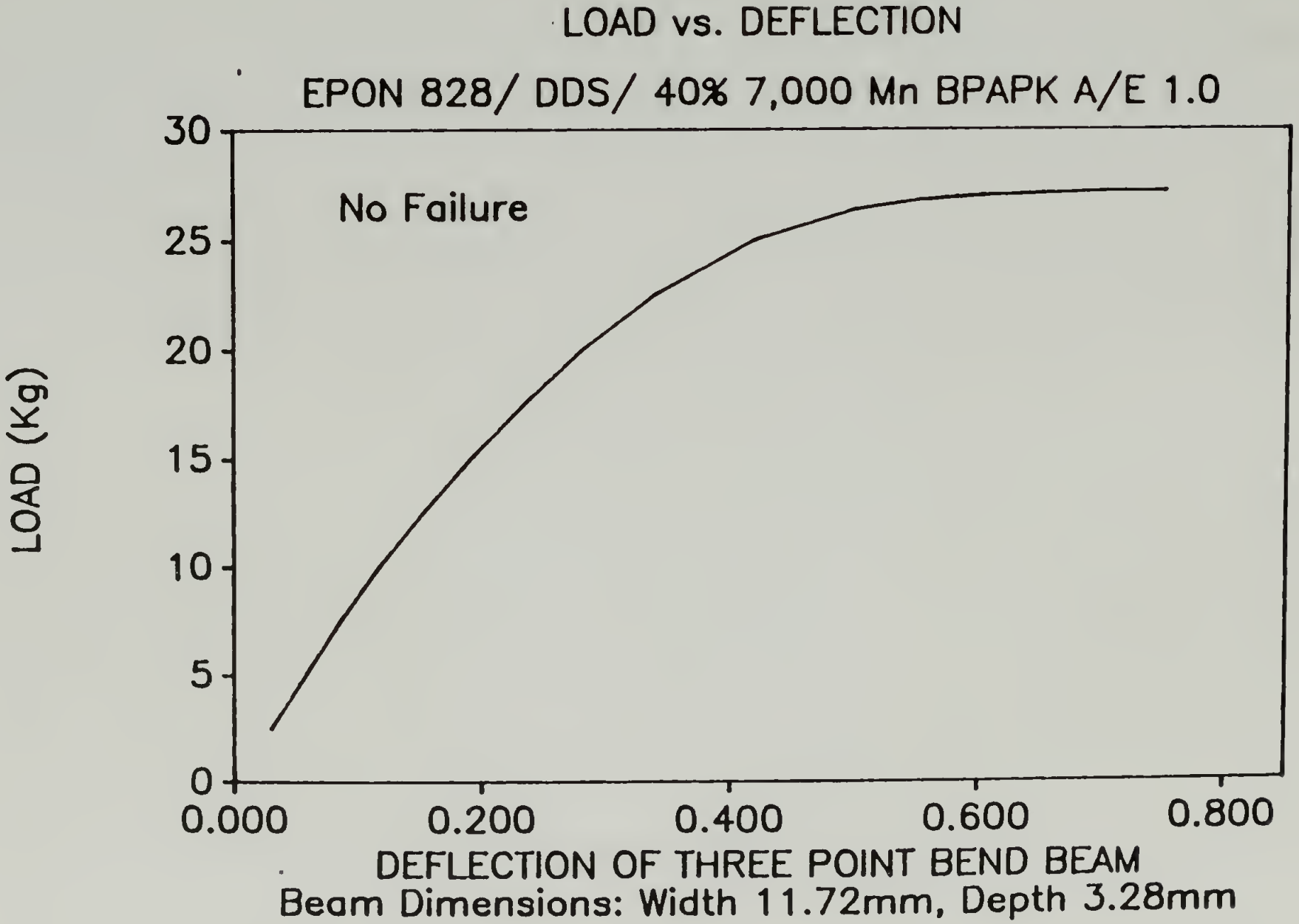


Figure 2.22 Load vs. Deflection of a three point bend beam of Epon 828/ DDS/ 40% 7,000 Mn BPAPK/ A/E = 1.0.

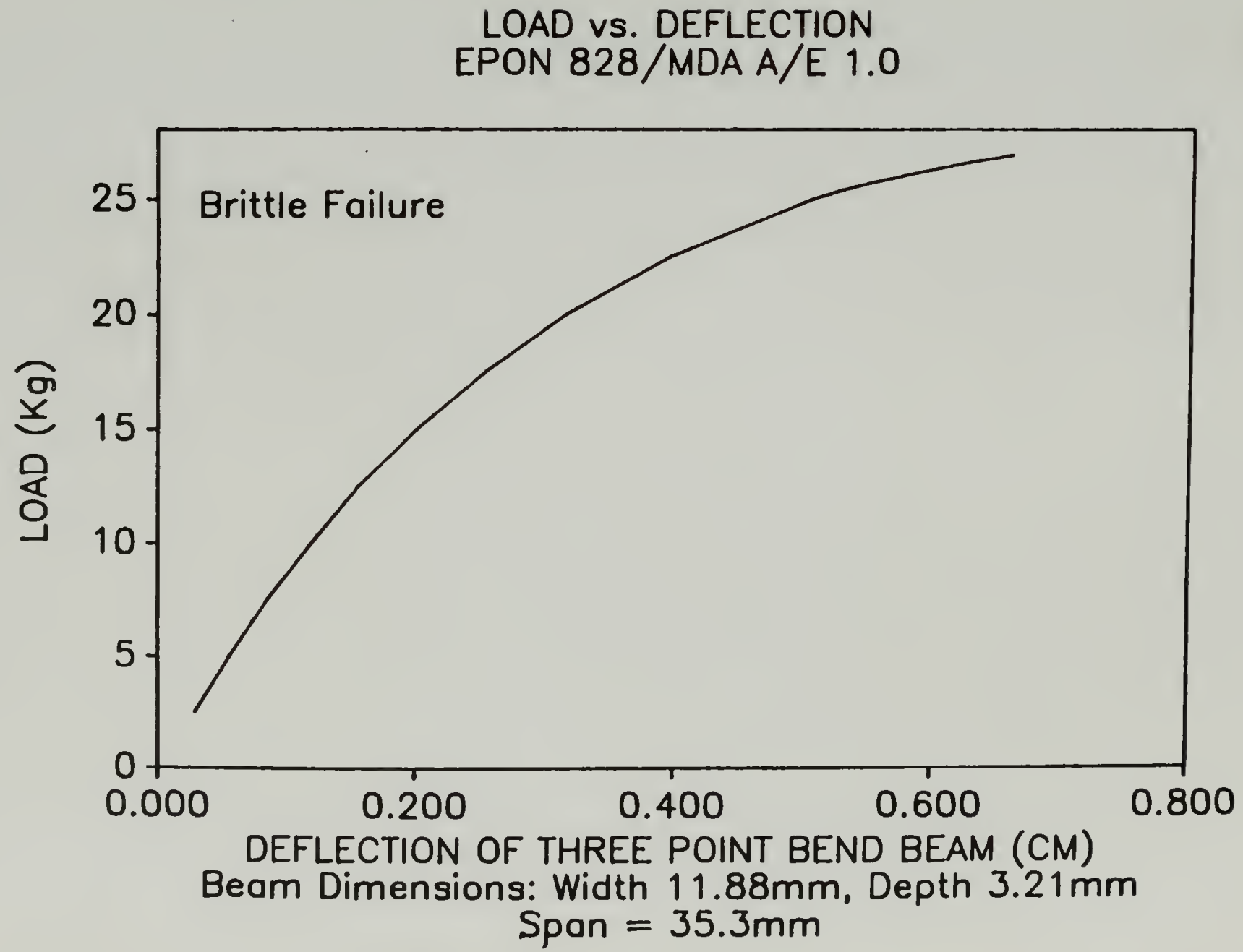


Figure 2.23 Load vs. Deflection of a three point bend beam of Epon 828/ MDA/ A/E = 1.0.

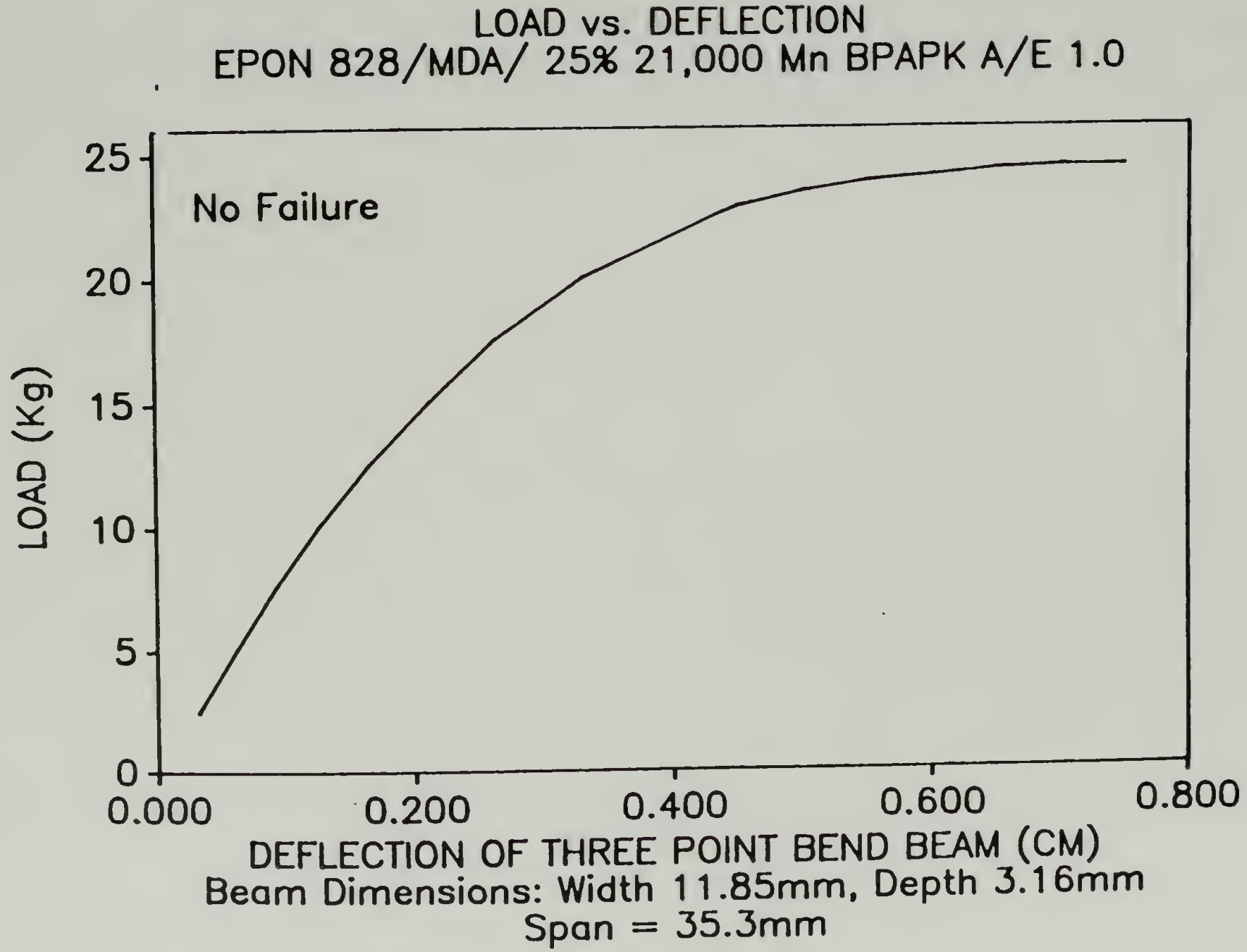


Figure 2.24 Load vs. Deflection of a three point bend beam of Epon 828/ MDA/ 25% 21,000 Mn BPAPK/ A/E = 1.0.

In Figure 2.19 the load vs. deflection curve for Epon 828 cured with DDS alone is represented. This material fails in a brittle manner exhibiting very little ductility. In Figure 2.20 the Epon 828/ DDS/ 20% by weight 7,000 Mn BPAPK sample also undergoes brittle failure with very little, if any ductility. In Figure 2.21 the Epon 828/ DDS/ 30% 7,000 Mn BPAPK sample exhibits ductility with the beam bending to a point where it's ends touched the loading platform without failing. Upon removal of the load from this beam a permanent set remained. On the tensile side of the beam at the central loading point a whitening of the material could be seen. The Epon 828/ DDS/ 40% 7,000 Mn BPAPK is represented in Figure 2.22. This load deflection curve is identical to that obtained at the 30% 7,000 Mn loading level. The 40% 7,000 Mn BPAPK sample also exhibits ductility, no failure, a permanent set in the unloaded beam, and whitening on the tensile side. Figure 2.23 shows the load deflection curve obtained for the Epon 828/ MDA sample. This figure shows some non linear behavior prior to a brittle failure. The Epon 828/ MDA/ 25% 21,000 Mn BPAPK load deflection curve is shown in Figure 2.24. This load deflection curve shows much more ductility than the neat resin (Figure 2.23) and no failure. This sample is similar to the 30 and 40% 7,000 Mn BPAPK samples in that a permanent set was observed after unloading of the beam. As a result of the green opaque nature of this sample, the presence or absence of whitening could not be ascertained.

In Figures 2.25-2.31, the dynamic mechanical storage and loss moduli, and loss factor are plotted versus temperature for the 7,000 Mn and the 21,000 Mn BPAPK formulations. Figures 2.25-2.27 represent the Epon 828/MDA/21,000 Mn BPAPK systems at 0, 10, and 20 percent by weight of the 21,000 Mn BPAPK respectively. Figures 2.28-2.31 represent the Epon 828/DDS/7,000 Mn BPAPK systems at 0, 20, 30, and 40 percent by weight 7,000 Mn BPAPK. In these formulations prepared at the lower loading level, two glass transition temperatures can be seen. At these higher molecular weights the phase separation should be more complete than that encountered with the 4,400 Mn oligomer leading to smaller amounts of the BPAPK in the epoxy rich phase. Therefore two distinguishable glass transitions are to be expected. At the higher loading levels only one glass transition temperature can be seen as a result of the tremendous drop in material stiffness at the first transition temperature and the inherent lack of sensitivity of the Dynastat on three point bend samples of this thickness.

In Figures 2.32 to 2.35, the transmission electron micrographs of these BPAPK formulations are represented. The TEM samples have been stained with osmium tetroxide which acts by combining with the double bonds in the phases (40). The double bond rich phase appears darker in the transmission electron micrograph as a result of the incorporation of a higher density of stain. The stain acts

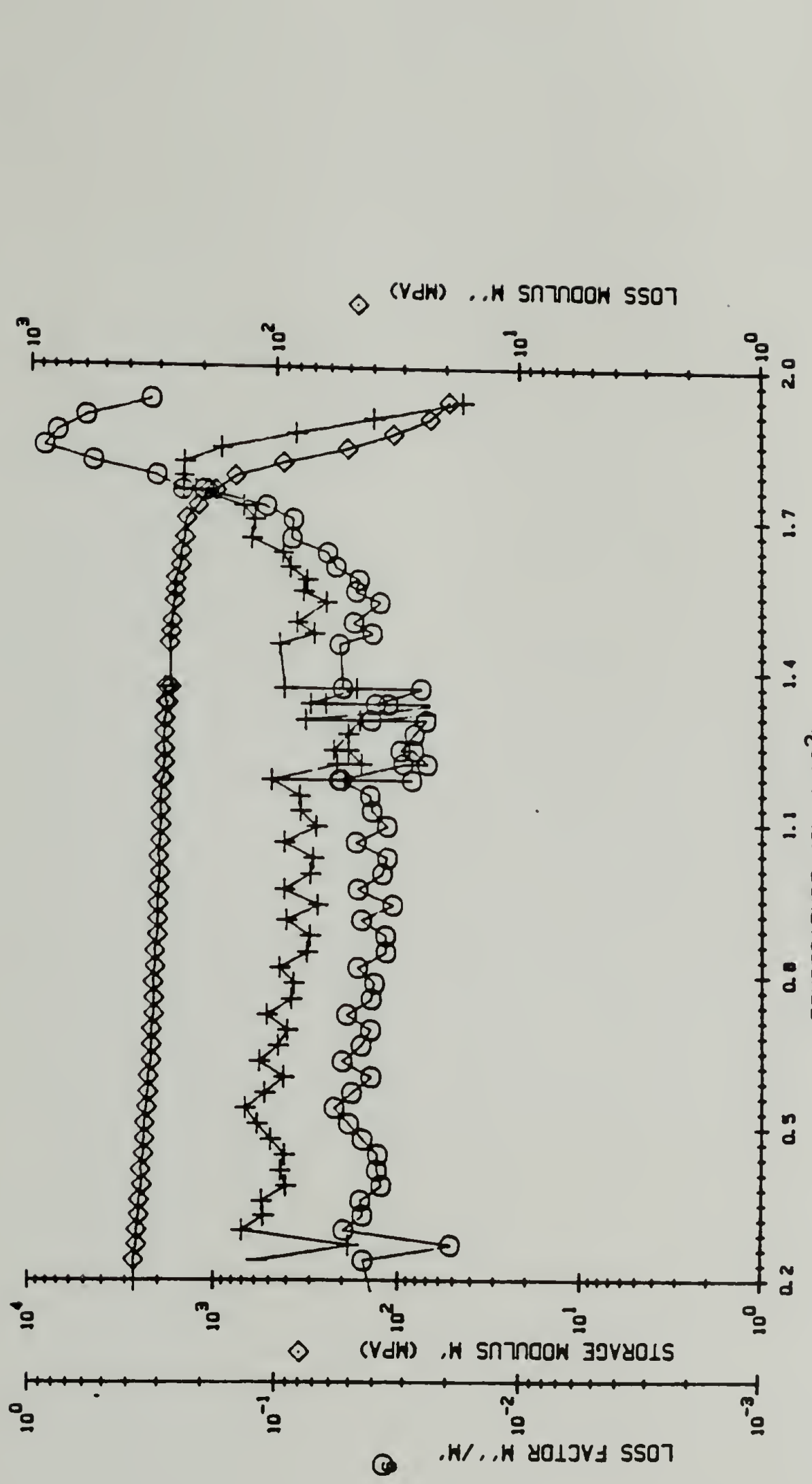


Figure 2.25 Dynamic Mechanical Properties of Epon 828/ MDA/ A/E = 1.0.

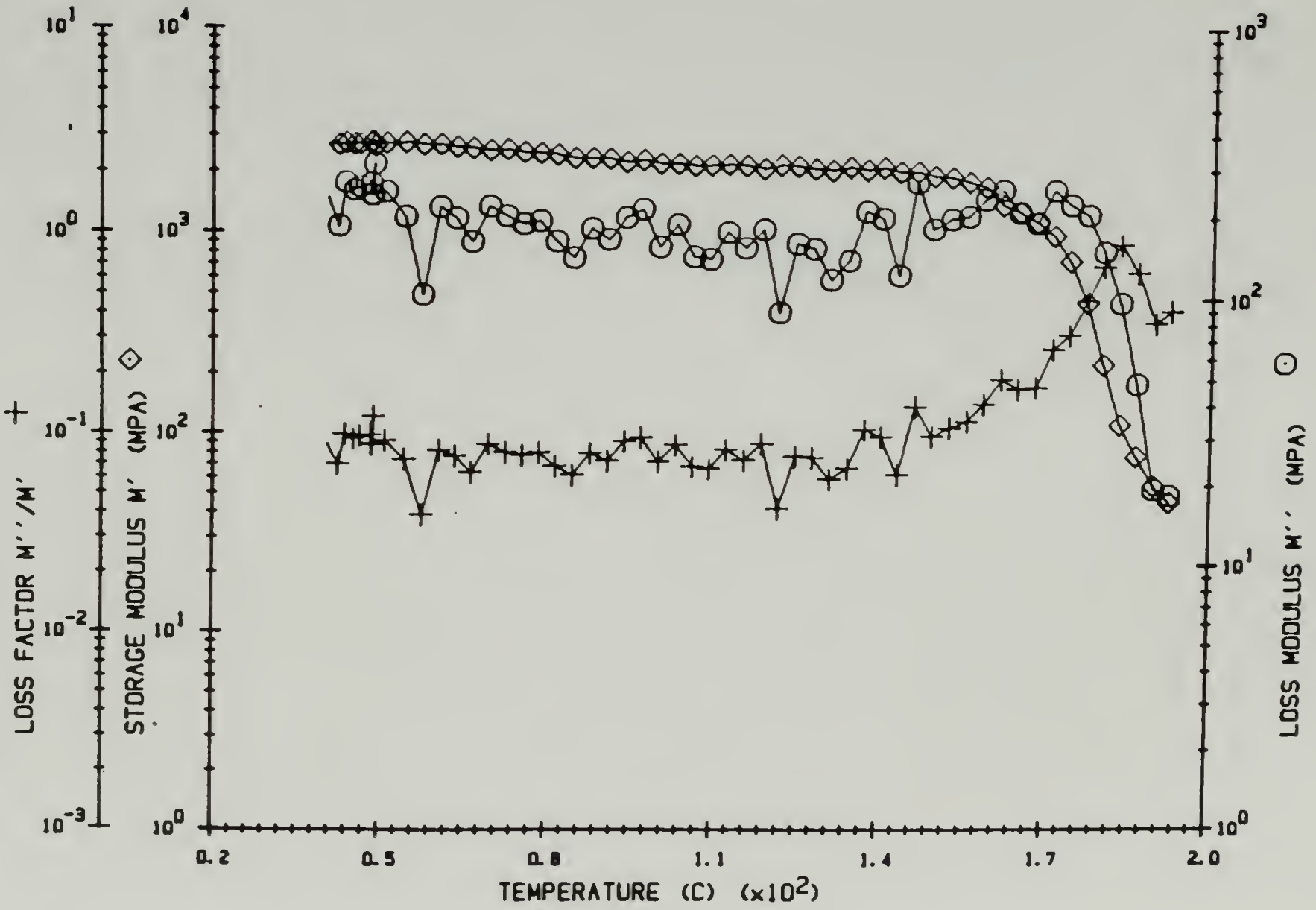


Figure 2.26 Dynamic Mechanical Properties of Epon 828/ MDA/ 10% 21,000 Mn BPAPK/ A/E = 1.0.

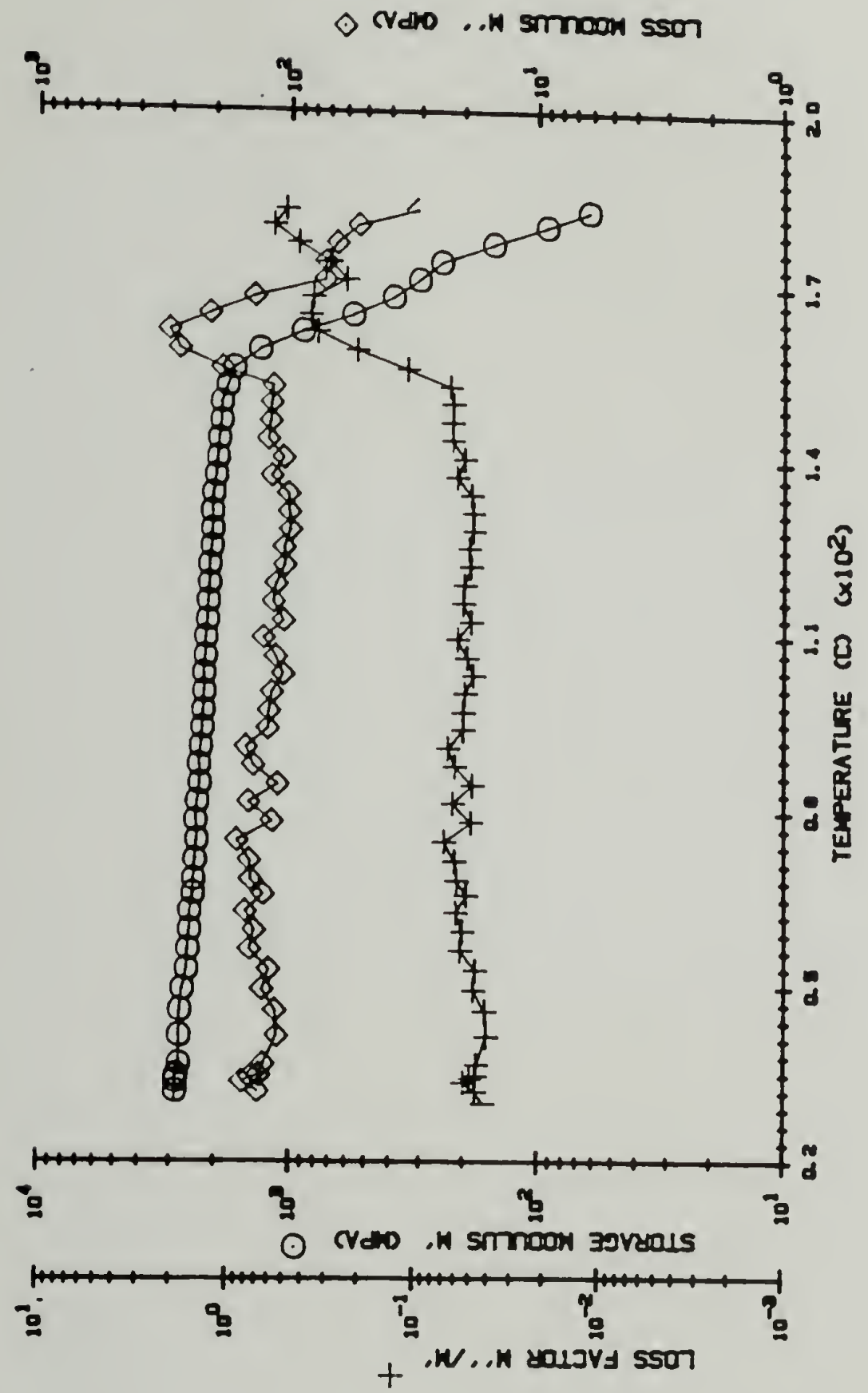


Figure 2.27 Dynamic Mechanical Properties of Epon 828/ MDA/ 20% 21,000 Mn BPAPK/ A/E = 1.0.

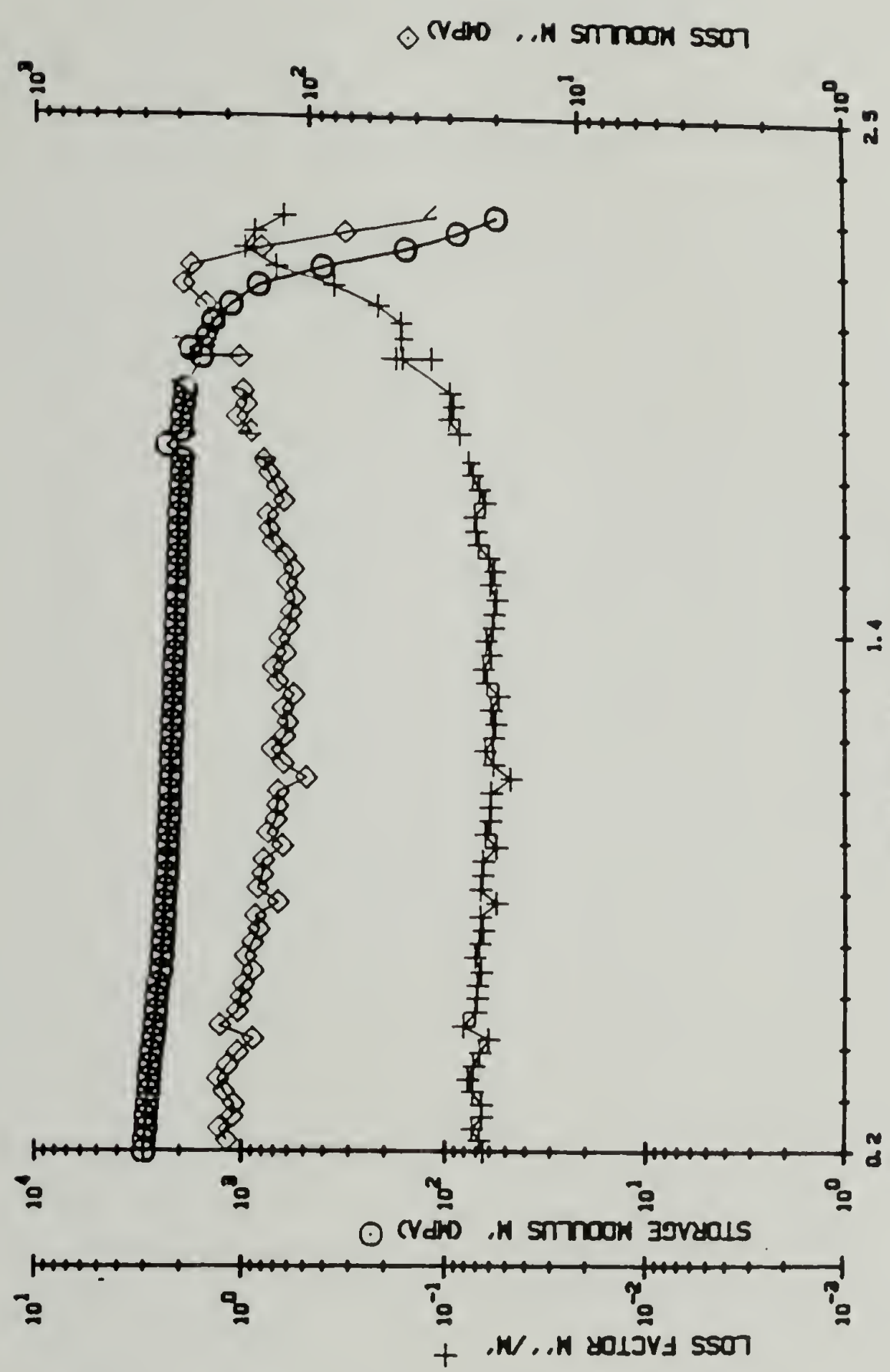


Figure 2.28 Dynamic Mechanical Properties of Epon 828/ DDS/ A/E = 1.0

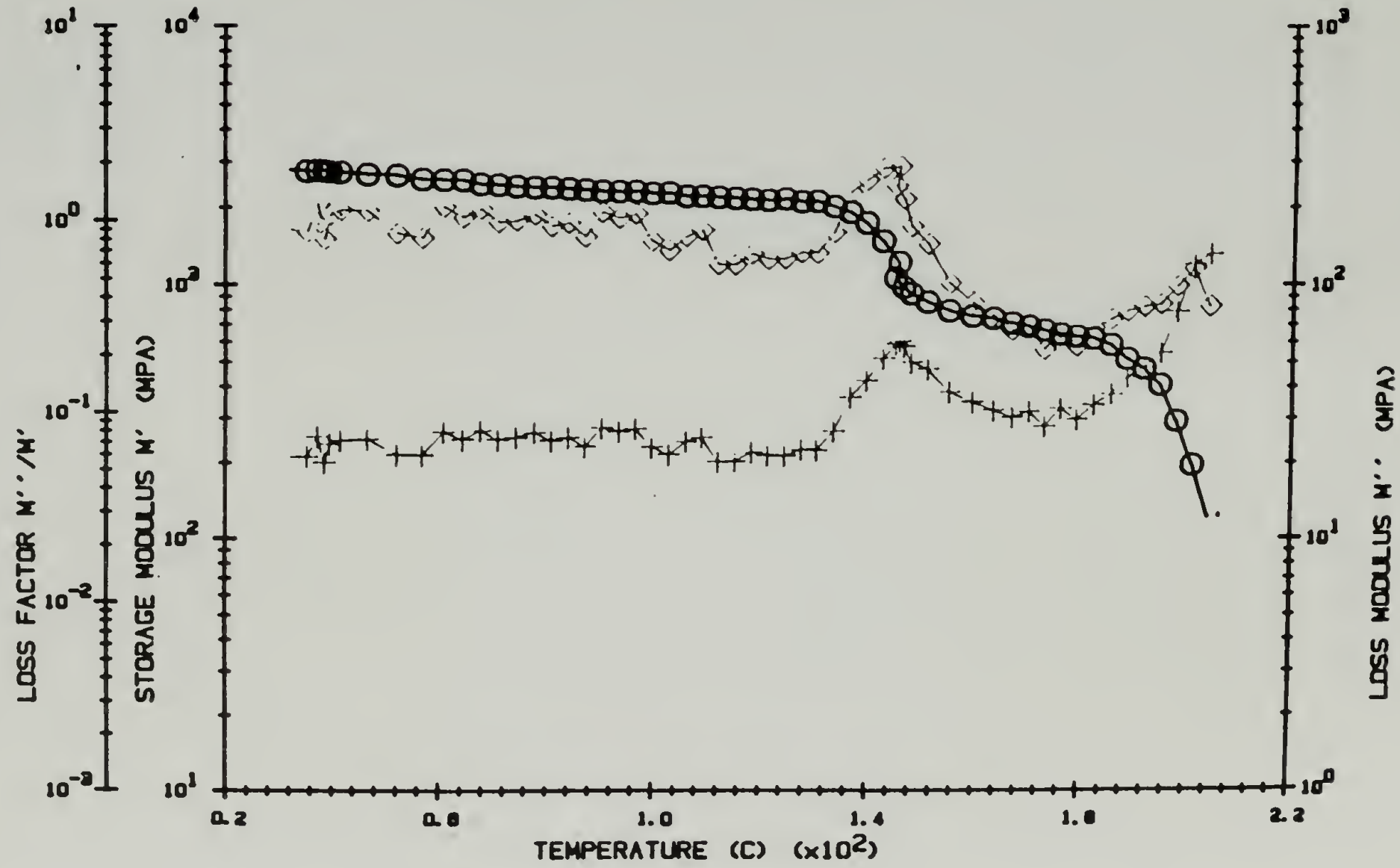


Figure 2.29 Dynamic Mechanical Properties of Epon 828/ DDS/ 20% 7,000 Mn BPAPK/ A/E = 1.0.

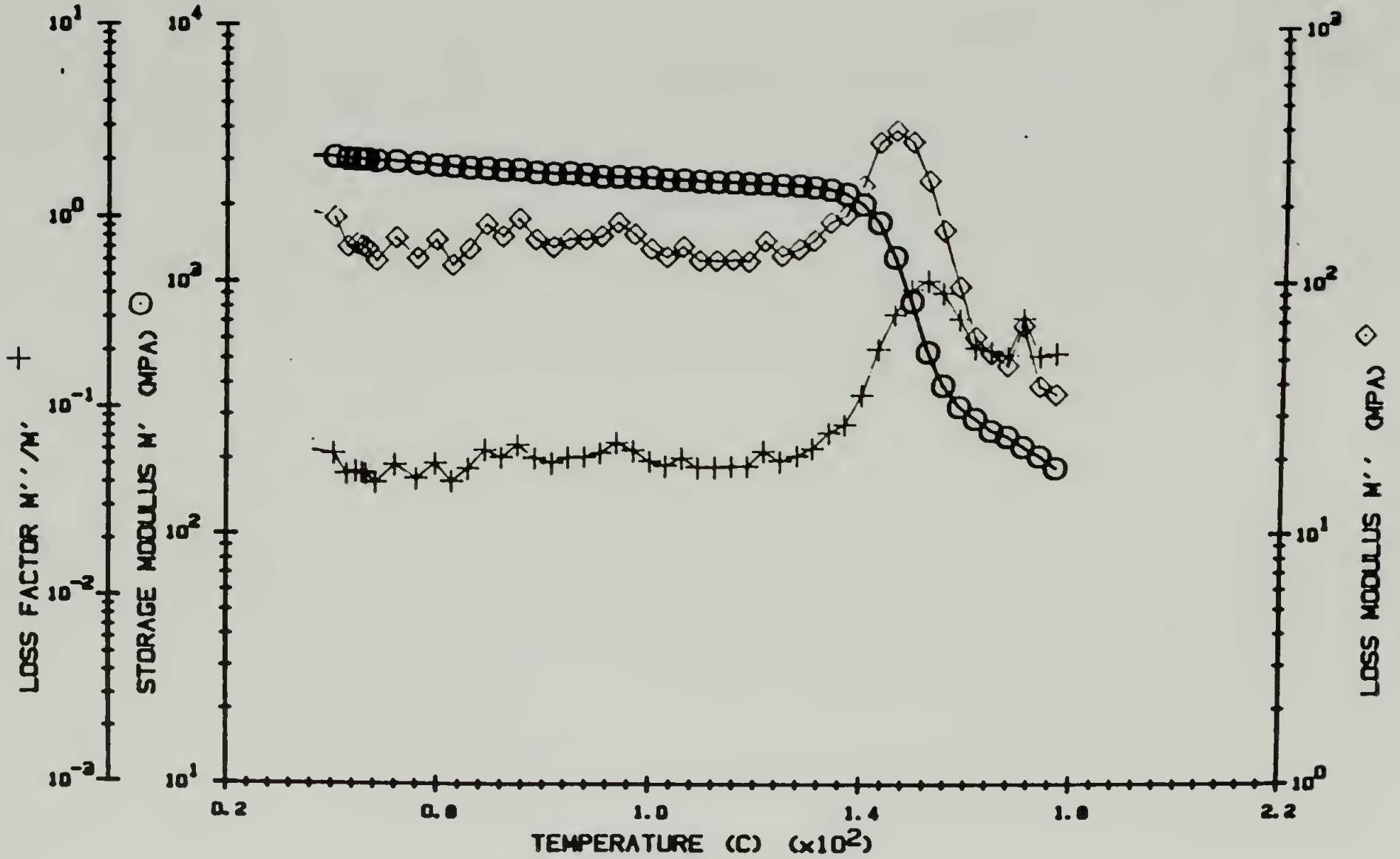


Figure 2.30 Dynamic Mechanical Properties of Epon 828/ DDS/ 30% 7,000 Mn BPAPK/ A/E = 1.0.

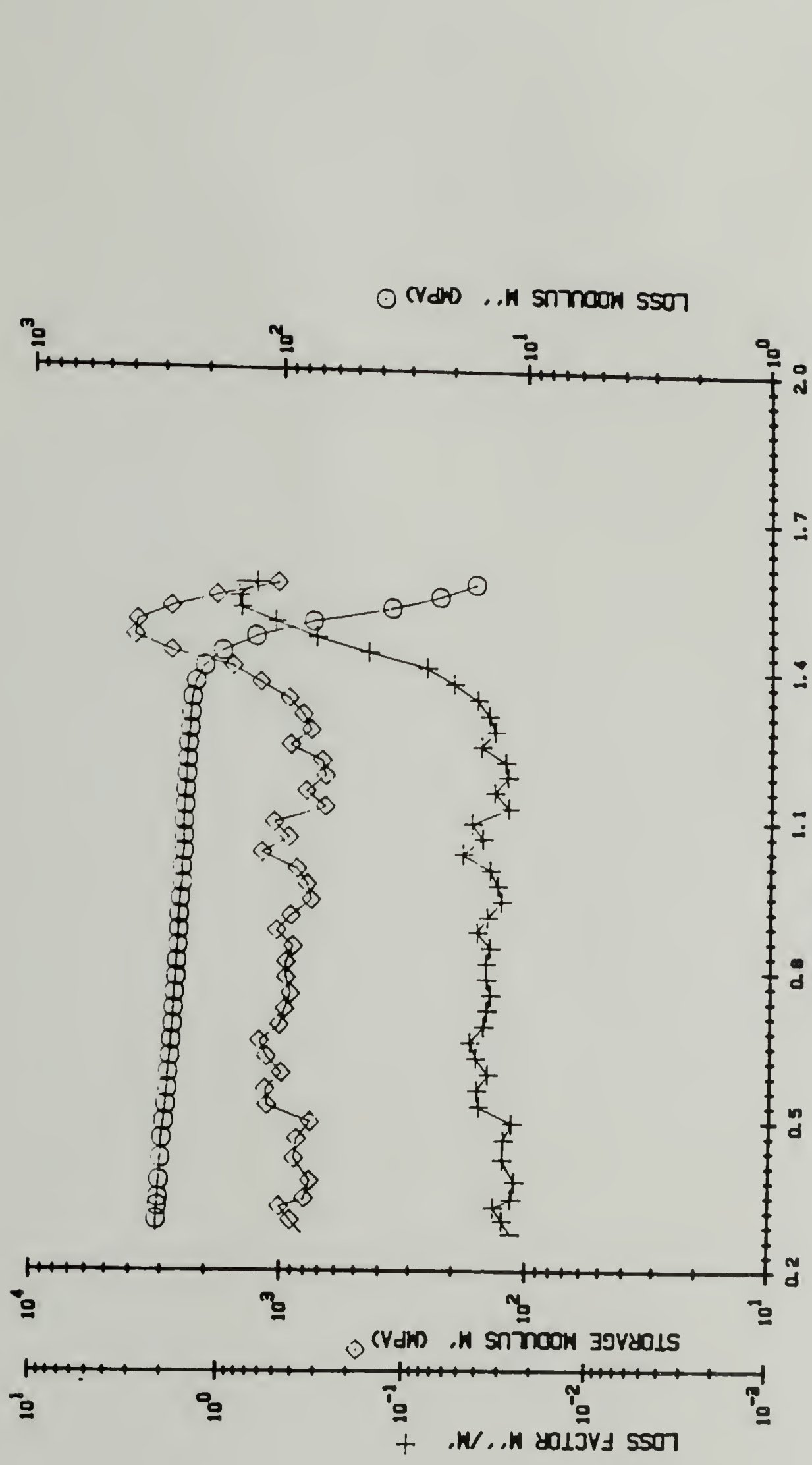


Figure 2.31 Dynamic Mechanical Properties of Epon 828/ DDS/ 40% 7,000 Mn BPAPK/ A/E = 1.0.

Figure 2.32B Transmission Electron Micrograph of Epon 828/ DDS/ 20% 7,000 Mn BPAPK/ A/E = 1.0.

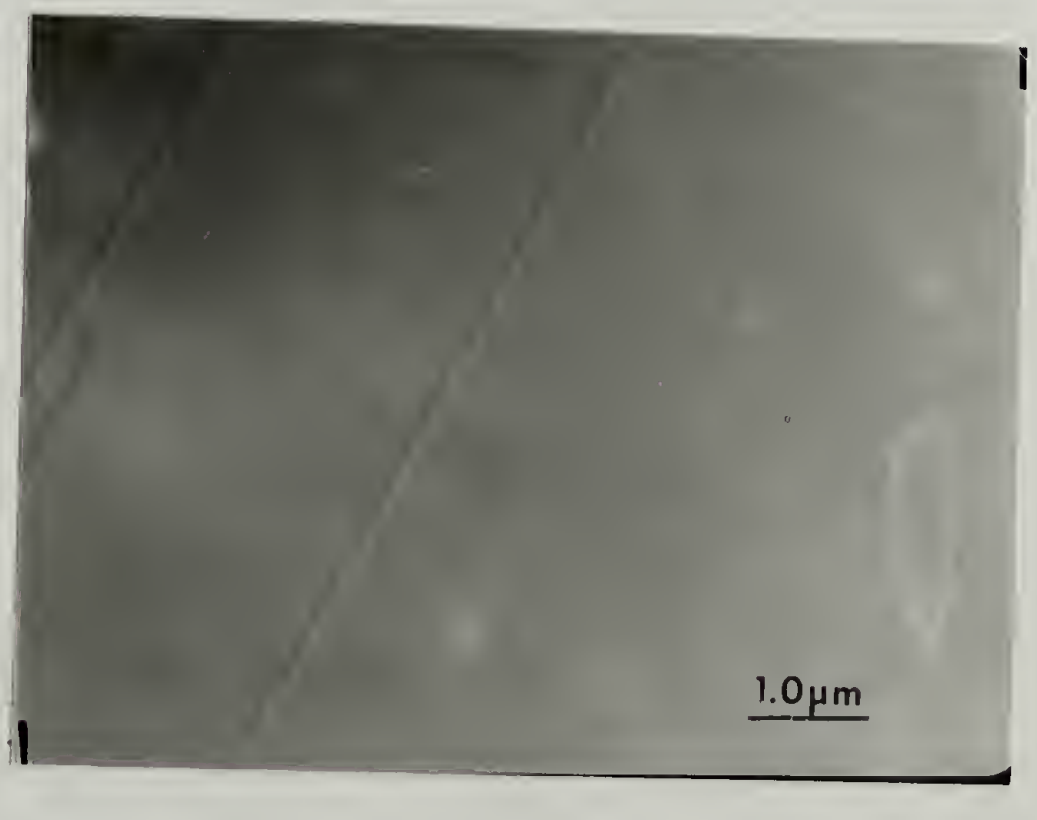


Figure 2.32A Transmission Electron Micrograph of Epon 828/ DDS/ A/E = 1.0.

Figure 2.33A Transmission Electron Micrograph of Epon 828/ DDS/ 30% 7,000 Mn BPAPK/ A/E 1.0.

Figure 2.33B Transmission Electron Micrograph of Epon 828/ DDS/ 40% 7,000 Mn BPAPK/ A/E 1.0.

Figure 2.34A Transmission Electron Micrograph of Epon 828/ MDA/ A/E 1.0.

Figure 2.34B Transmission Electron Micrograph of Epon 828/ MDA/ 10% 21,000 Mn BPAPK/ A/E 1.0.

Figure 2.35 Transmission Electron Micrograph of Epon 828/ MDA/ 25% 21,000 Mn BPAPK/ A/E 1.0.

to impede the transmission of the electron beam through the sample by increasing the electron density of that phase. Since both phases contain double bonds stain absorption/reaction should be expected in both however the BPAPK contains a 40% higher double bond density than the epoxy resin and therefore that phase would be expected to be darker. The calculation of the double bond densities assumes that one phase is BPAPK and the other is epoxy and DDS each having similar specific gravities. In figure 2.32 and 2.33 the TEM micrographs of the Epon 828/ DDS/ 7,000 Mn BPAPK modifier at 0, 20, 30 and 40% by weight 7,000 Mn BPAPK are shown. In Figure 2.32A the micrograph of the Epon 828/ DDS sample shows that no phase morphology is seen after staining with osmium tetroxide (as expected). In Figure 2.32B the micrograph of the Epon 828/ DDS/ 20% 7,000 Mn BPAPK sample shows phase separation into an epoxy/ DDS rich continuous phase with spherical 1.2 to 3.6 micron diameter BPAPK rich inclusions. Figure 2.33A and 2.33B show the Epon 828/ DDS/ 30% and 40% 7,000 Mn BPAPK samples respectively. A phase inversion has occurred at the 30 and 40% loading levels. The 30% 7,000 Mn has a BPAPK rich continuous phase with 4 to 6 micron epoxy rich inclusions. The 40% 7,000 Mn also has a BPAPK rich continuous phase having 2.4 to 3.6 micron diameter spherical epoxy/ DDS rich inclusions. In Figures 2.34 and 2.35 the micrographs of the Epon 828/ MDA/ 21,000 Mn BPAPK are shown. Figure 2.34A demonstrates that no phase morphology is observed in the Epon 828 cured with

MDA alone (as expected). Figure 2.34B, a micrograph of the Epon 828/ DDS/ 10% 21,000 Mn BPAPK shows that this sample morphology consists of an epoxy/ MDA rich continuous phase with spherical BPAPK rich .2 to .5 micron spherical inclusions. The Epon 828/ DDS/ 25% 21,000 Mn BPAPK sample in Figure 2.35 shows that a phase inversion has occurred at this loading level. The BPAPK rich phase is now the continuous phase having 1.5 to 3 micron diameter spherical epoxy/ MDA rich inclusions.

In figures 2.36 and 2.37, the scanning electron micrographs of fracture surfaces are represented. In figure 2.36 the fracture surfaces of the Epon 828/DDS neat resin, Epon 828/20% 7,000 Mn BPAPK/DDS and Epon 828/40% 7,000 Mn BPAPK/DDS modified resins having fracture energies of 300 J/M^2, 900 J/M^2, and 2,300 J/M^2 respectively are shown. A correlation between G_{Ic} and fracture surface topography can be made. The micrograph of the neat resin fracture surface at 1000X is featureless, suggesting a smooth fracture surface and brittle failure. The micrograph of the 40% 7,000 Mn BPAPK formulation at the same magnification shows extensive tearing of the fracture surface. This extremely tough sample in fact exhibits extensive stress whitening of the fracture surface which is visible with the naked eye. The micrograph of the 20% 7,000 Mn BPAPK formulation at 100X shows what appears to be large torn, rough features in an otherwise featureless background. The fracture surface of this formulation does not exhibit stress whitening. This

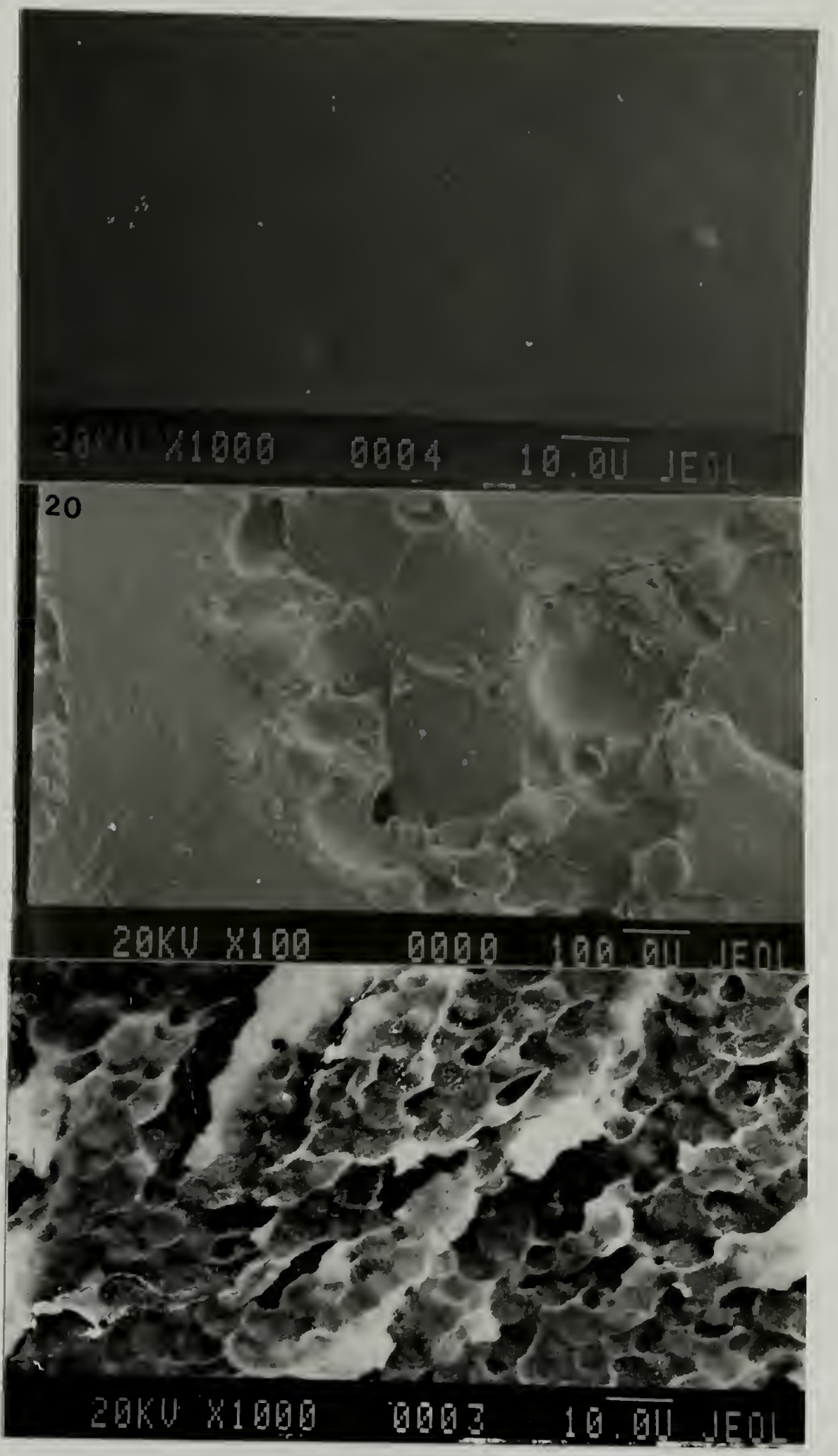
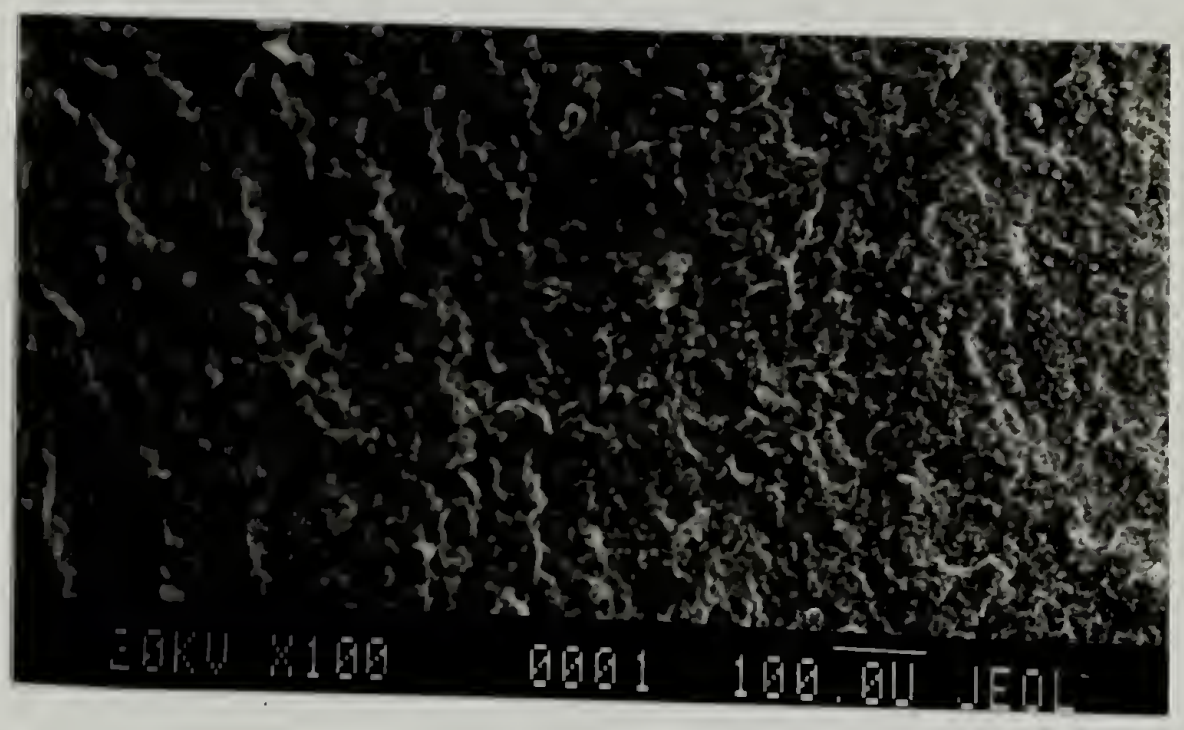


Figure 2.36 Scanning Electron Micrographs of Epon 828/ DDS/ A/E 1.0, Epon 828/DDS/ 20% 7,000 Mn BPAPK/ A/E 1.0, and Epon 828/ DDS/ 40% 7,000 Mn BPAPK fracture surfaces.



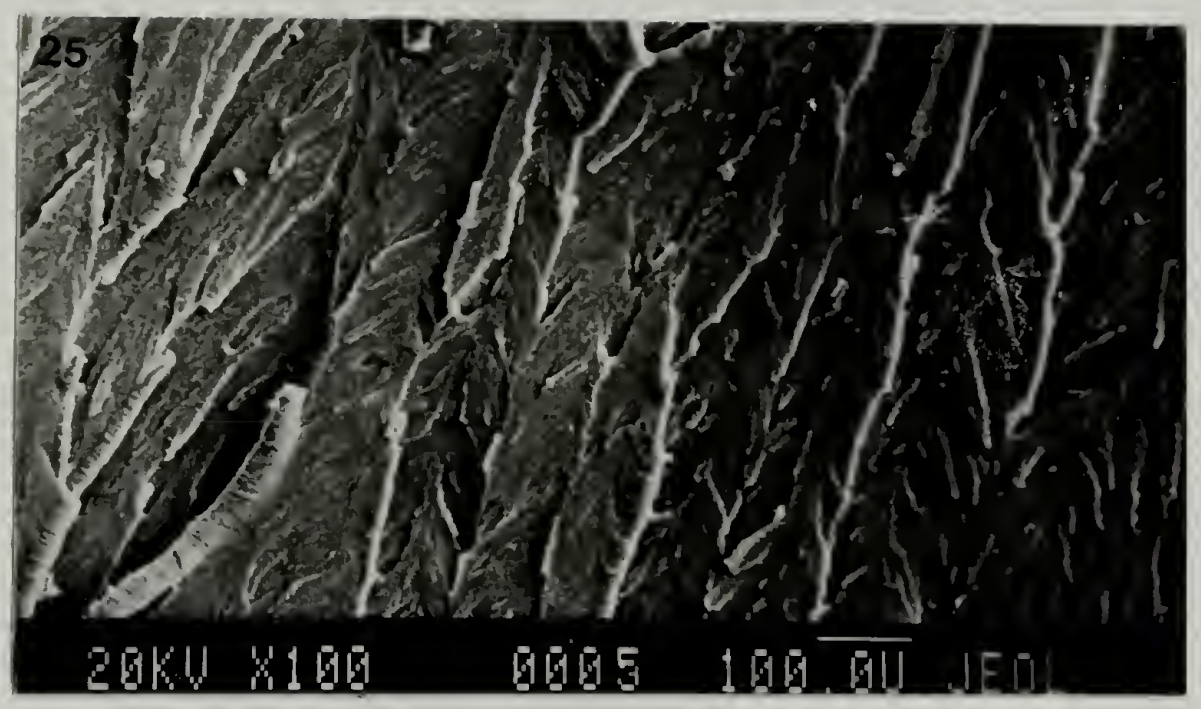


Figure 2.37 Scanning Electron Micrograph of Epon 828/ MDA/ A/E 1.0, 10% 21,000 MN BPAPK, and 25% 21,000 Mn BPAPK fracture surfaces.

20% loading is below the phase inversion level and the rough features may represent the fracture areas around the BPAPK rich areas. Note that the size of these features is much too large to be the BPAPK region alone. In figure 2.37 the micrographs of the Epon 828/MDA, Epon 828/10% 21,000 Mn BPAPK/MDA, and Epon 828/25% 21,000 Mn BPAPK/MDA fracture surfaces are shown. These systems have fracture energies of 300J/M^2, 517 J/M^2, and 1,350 J/M^2 respectively. Again a correlation between fracture surface roughness and fracture energy is observed. It is interesting to note the apparent orientation in these fracture surface features with respect to that seen in the 7,000 Mn BPAPK systems. This orientation may be the result of molecular orientation in the fracture sample due to either the effect of the higher molecular weight during sample preparation or orientation of higher molecular weight polymer molecules during the application of the fracture stress.

The solvent absorption of the BPAPK containing formulations was also investigated using solvents listed in a Boeing specification for aerospace applications. In figures 2.38 to 2.41, the solvent absorption data for the neat resins, the 40% 7,000 Mn BPAPK/ Epon 828 /DDS system, and the 25% 21,000 Mn BPAPK / Epon 828 / MDA system is shown. The details of the solvent absorption test are located in appendix 5. In figure 2.38 the absorption of water is shown. The Epon 828/ DDS/ 40% 7,000 Mn BPAPK sample absorbed approximately 50% less water than the neat

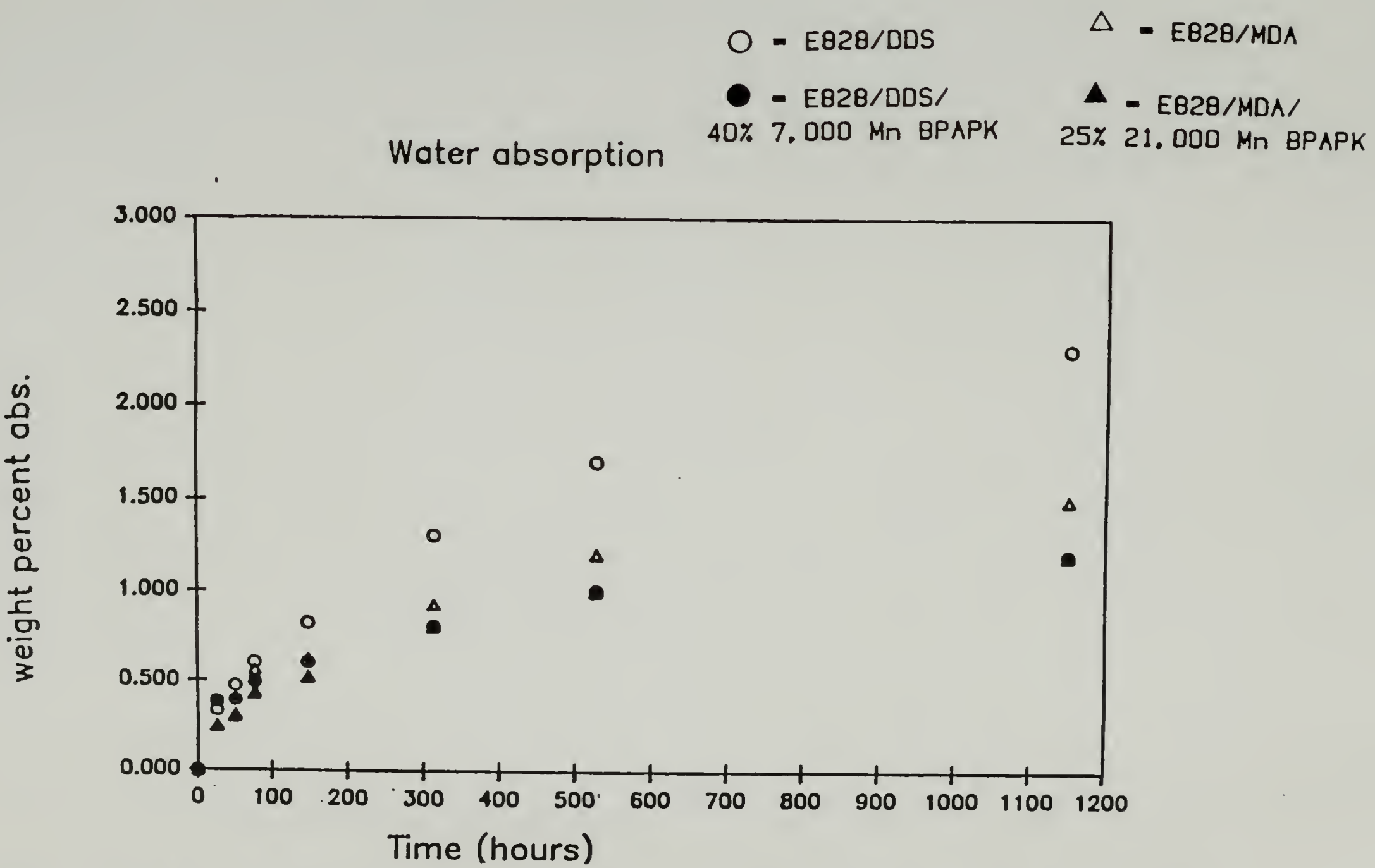


Figure 2.38 Water absorption of Epon 828/ DDS, Epon 828/ DDS/ 40% 7,000 Mn BPAPK, Epon 828/ MDA, and Epon 828/ MDA/ 25% 21,000 Mn BPAPK samples.

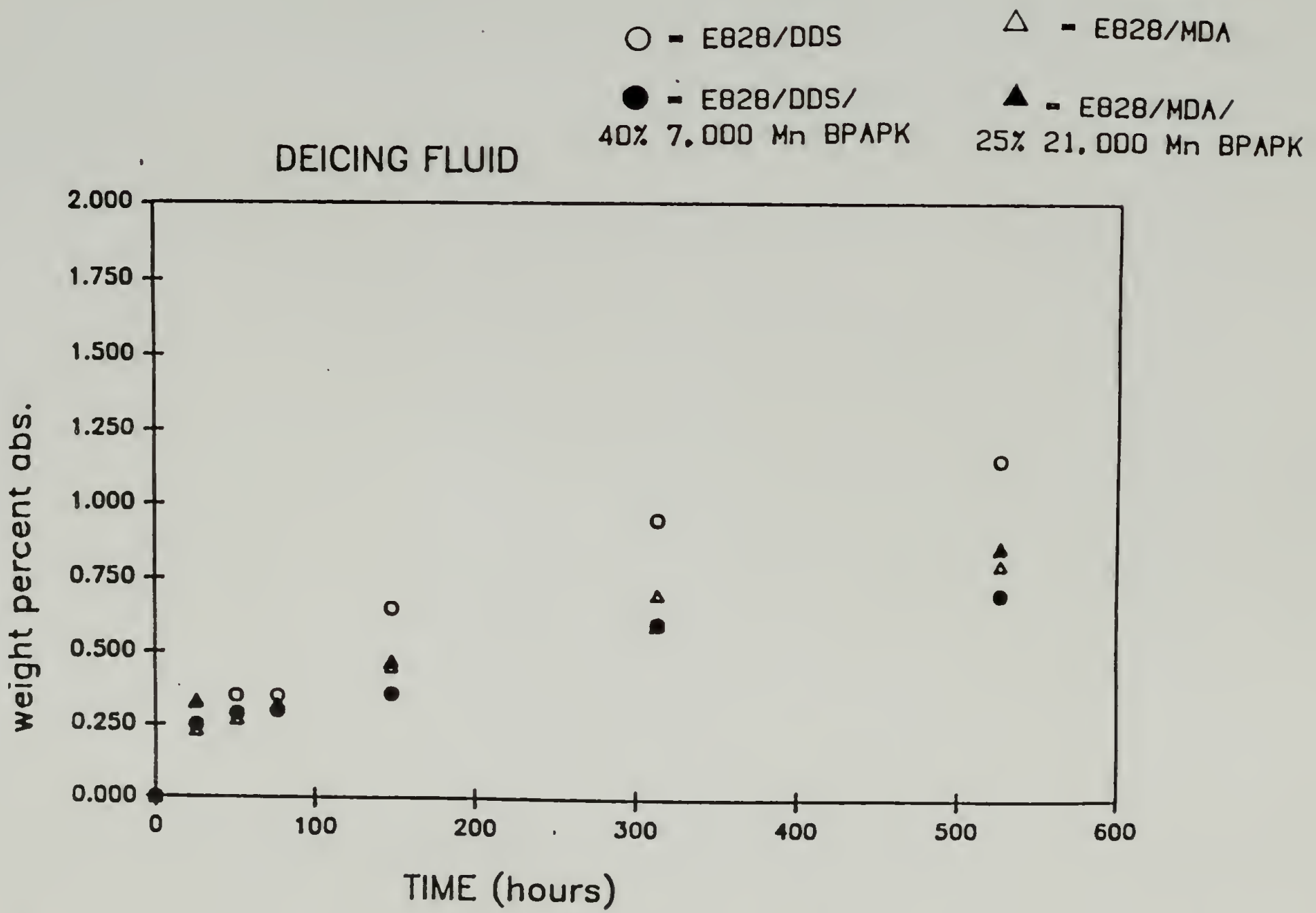


Figure 2.39 Deicing fluid absorption of Epon 828/ DDS, Epon 828/ DDS/ 40% 7,000 Mn BPAPK, Epon 828/ MDA, and Epon 828/ MDA/ 25% 21,000 Mn BPAPK samples.

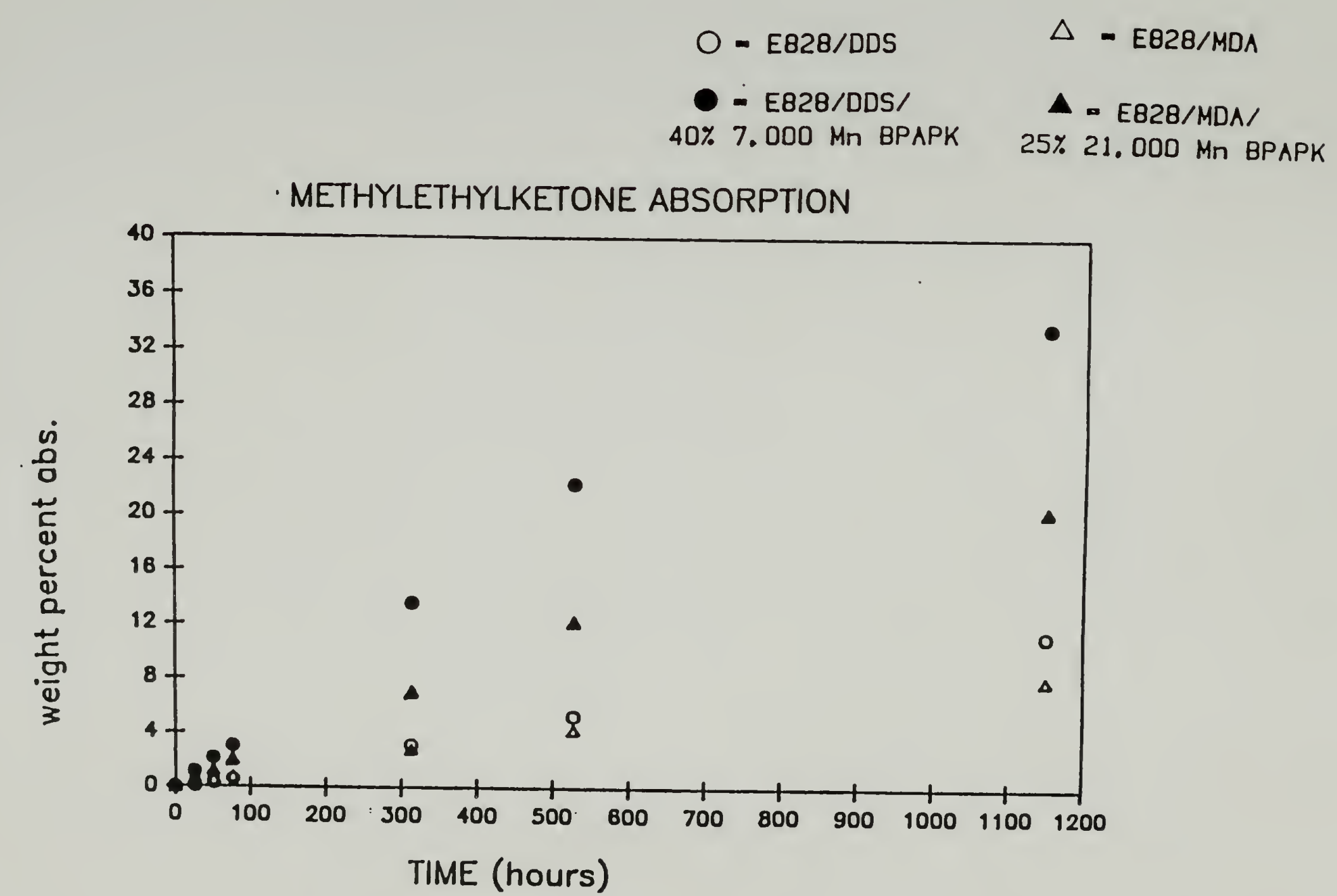


Figure 2.40 Methylene chloride absorption of Epon 828/ DDS, Epon 828/ DDS/ 40% 7,000 Mn BPAPK, Epon 828/ MDA, and Epon 828/ MDA/ 25% 21,000 Mn BPAPK samples.

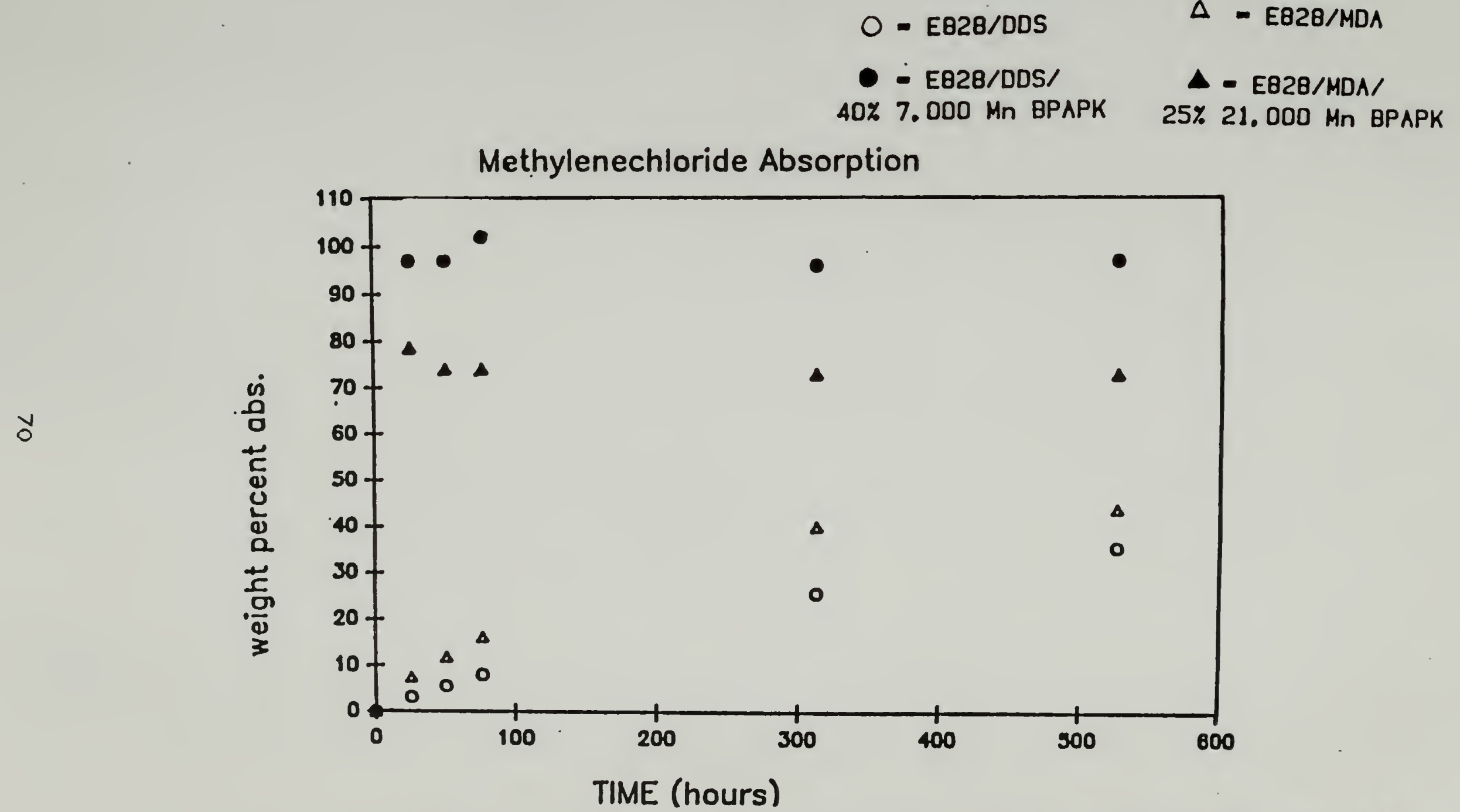


Figure 2.41 Methylethylketone absorption of Epon 828/ DDS, Epon 828/ DDS/ 40% 7,000 Mn BPAPK, Epon 828/ MDA, and Epon 828/ MDA/ 25% 21,000 Mn BPAPK samples.

resin while the Epon 828/ MDA/ 25% 21,000 Mn BPAPK sample absorbed approximately 25% less than it's corresponding neat resin after 1200 hours of immersion. In figure 2.39 the absorption of deicing fluid is reported. Once again the Epon 828/ DDS/ 40% 7,000 Mn BPAPK formulation absorbed considerably less than the corresponding neat resin while the Epon 828/ MDA/ 25% 21,000 Mn BPAPK sample absorption was identical to that of the neat resin. The absorption of Jet fuel JP5 and Skydol hydraulic fluid was negligible for all of the formulations tested, modified resins and neat resins alike. In figure 2.40 the absorption of methylene chloride is reported. This solvent is the "Achilles' Heel" of these BPAPK containing materials. The modified resins absorb 80% to 100% by weight methylenechloride in less than 24 hours while the neat resins absorb less than 8% in the same time period. After 500 hours the BPAPK modified formulations absorbed approximately 2 times that of the neat resins. Upon evaporation of the methylene chloride from the solvent sample vial, evidence for a very small soluble fraction is found for both the modified resins and the neat resins. In Figure 2.41 the absorption of methyl ethyl ketone is reported. The BPAPK modified formulations once again absorb considerably more than the neat resins and at a much faster rate. After 1200 hours the BPAPK containing samples had absorbed 34% and 20% respectively while the corresponding neat resins had absorbed 11% and 8% respectively.

2.4 Conclusions

A tough matrix material can be achieved via the incorporation of an oligomeric end functionalised bisphenol A polyetheretherketone into a commercial epoxy resin while maintaining processability. Higher molecular weight functionalised oligomers yield higher K_{Ic} values. The substantial increase in resistance to fracture, while maintaining a modulus of 2-3 Gpa makes these materials very attractive for composite use.

These BPAPK systems behave similarly to the amine terminated polyethersulphone (ATPEES)/ epoxy systems (23-26). TEM micrographs of the modified resins have shown conclusively that phase separation does occur in these materials upon cure. Evidence for a phase inversion at the higher loading levels has also been found. At the lowest loading level (20% of 7,000 Mn and 10% of 21,000 Mn BPAPK) the morphology consists of an epoxy rich continuous phase and BPAPK rich inclusions. At the next highest loading levels their is a phase inversion leading to a BPAPK rich continuous phase having epoxy/ curing agent rich inclusions. The phase inverted systems have domain sizes which are compatible with composite inter-fiber spacing. In this BPAPK rich continuous phase morphology the size of the domains is not as important in allowing for ductility in the matrix as it is in epoxy rich continuous phase systems. The BPAPK continuous phase should be capable of absorbing large

amounts of energy prior to failure as long as the epoxy rich inclusion size is not so large that a catastrophic flaw is produced.

K_{Ic}, G_{Ic}, and ductility of these samples can be correlated to phase morphology. Maximum toughness and ductility are attained only when the continuous phase is BPAPK rich. In the epoxy/curing agent rich continuous phase the BPAPK rich inclusions act as stress concentrators in the matrix. As a result of the similar tensile, shear, and bulk moduli of the two phases these stress concentrations should be very small. The stress concentrations may cause the initiation of more extensive localized shear yielding in the matrix than that found in the neat resin resulting in slight increases in the resistance to crack propagation. These inclusions also have the ability to deform in a ductile manner, thereby increasing the energy required for crack propagation further. Due to incomplete phase separation, the epoxy rich continuous phase also has some BPAPK oligomer which acts to increase the average molecular weight between crosslinks. This greater distance between crosslinks allows for more energy absorbing motion prior to failure than that of the epoxy neat resin and therefore significant improvements in fracture resistance may be observed. At the higher loading levels there is a phase inversion in which the inclusions are now epoxy/curing agent rich and the matrix is BPAPK rich. In this morphology, the distance between crosslinks in the matrix (continuous phase) is

greatly increased, allowing for the chain mobility required for large energy absorbing deformations. Therefore at these high loading levels the inherent level of ductility of the material is greatly increased and is responsible for the observed tremendous increases in resistance to fracture. Deformations become similar to those found in the parent aromatic thermoplastic material. The SEM micrographs of the fracture surfaces as well as the load deflection curves of the toughest fracture samples strongly indicate ductile failure. The presence of the phase inverted morphology also explains the solvent absorption behavior. The behavior of the highest loading levels mimics that of the BPAPK homopolymer. In this phase inverted morphology the matrix material can be more correctly considered a "processable, thermosetting bisphenol A PEEK " rather than a toughened epoxy. The glass transition temperatures (Tg) of the modified Heloxy 69 and Epon 828 resins at an amine to epoxy ration of 1.2 are too low for high performance composite use. At an amine to epoxy ratio of 1.0 an increase in the Tg of 25° C is obtained. At this stoichiometry the modified resins have glass transition temperatures which are sufficient for high performance composite applications. The K_{Ic} and G_{Ic} values obtained are the highest reported for any thermoset system having a glass transition temperature of greater than 140° C.

In conclusion, while others have demonstrated the ability of this technique to improve the mechanical

properties of matrix resins, until now there has been no published information other than patent literature on the ability to produce formulations which are processable via conventional methods. The formulations in Table 2.2 represent the toughest, processable, high glass transition thermosetting matrix resins developed to date. The SEM, TEM, and solvent resistance data have helped to elucidate the mechanism by which these resin formulations achieve such high levels of toughness.

Chapter 3

HYDROQUINONE BASED POLYARYLETHERKETONE AS A MATRIX MODIFIER WITH COMMERCIAL EPOXY RESINS

3.1 Introduction

The polyaryletherketone made from the reaction of hydroquinone and 4,4´-difluorobenzophenone is an extremely tough semicrystalline material having a glass transition temperature of 143°C and a crystalline melt temperature of 325°C (41). The structure of this polymer in the amine-terminated form is shown in figure 3.1. As a result of the crystalline nature of this polymer it has much better solvent resistance than any of it´s amorphous polyaryletherketone counterparts (42). No work involving the amine functionalisation of this polymer or it´s use as a reactive ingredient in an epoxy resin formulation has been reported in the literature. This lack of published work is no doubt a result of the difficulties encountered in working with this high melting polymer.

Despite the difficulties anticipated with hydroquinone polyetheretherketone (HDQPK), it was hoped that crystallization would occur in the HDQPK rich phase of a phase separated resin formulation when the HDQPK component was of sufficiently high molecular weight. In this morphology the HDQPK would be expected to impart to the

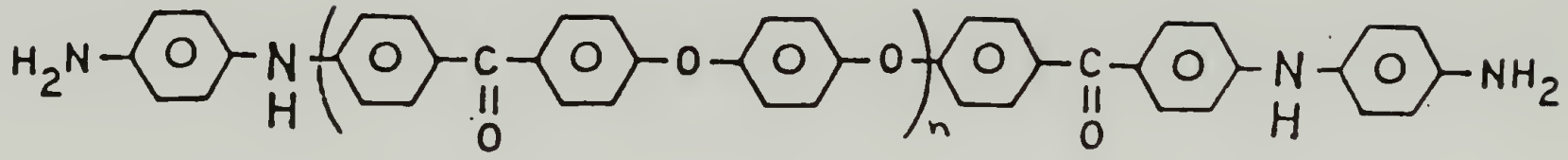


Figure 3.1
HYDROQUINONE POLYETHERETHERKETONE

resin the improved solvent resistance associated with the crystalline material. In the phase inverted morphology, where the HDQPK becomes the continuous phase, excellent solvent resistance should be attained.

The high melt temperature of HDQPK precludes dissolution in all but strong acids at room temperature (43). This polymer is soluble in a variety of solvents above 200° C, however these extraordinarily high temperatures prevent the use of the standard amine termination method used on the BPAPK. Reactions at this temperature would include the reverse attack of the 4-aminophenol leading to phenol terminated polymer having sterically hindered secondary aromatic amine groups (34). A second side reaction also is present, occurring to a greater extent than displacement of the halide end groups. This side reaction involves attack by the primary aromatic amines at the carbonyls along the polymer backbone leading to hemiaminal formation which upon further heating eliminate water to form very stable Schiff bases (44). As a result of these temperature imposed reaction difficulties, a different technique was developed to amine terminate the polymer. This technique allowed for the displacement of the halide end groups without the undesirable formation of the Schiff bases along the polymer backbone. Unfortunately, the formation of the hemiaminals could not be avoided. A simple technique was used to remove these hemiaminals without disturbing the end groups. The reaction temperature had to

be restricted to 190°C to prevent the conversion of the hemiaminals to Schiff bases which cannot be removed easily. This ceiling temperature limited the molecular weight of the HDQPK which could be synthesized. In the N-methylpyrrolidinone / toluene reaction mixture the HDQPK precipitated from solution at a number average molecular weight of 1,200 grams per mole.

3.2 Experimental

Potassium carbonate, potassium hydroxide, hydroquinone, 4,4´-dichlorobenzophenone, 4,4´difluorobenzophenone, 1,4-phenylenediamine, and diamino diphenyl sulphone (DDS) were obtained from Aldrich Chemical Company in the highest purity available. Epon 828, Heloxy 69, and MY720 were obtained from Shell Chemical Company, Wilmington Chemical Company, and Ciba Geigy respectively. N-methylpyrrolidinone was vacuum distilled from P_2O_5 and stored under nitrogen. Toluene was distilled from CaH_2 and stored under nitrogen.

3.2.1 Synthesis of Oligomeric Aromatic Amine-terminated Polyaryletherketone

Both the polymerization and endcapping reactions are nucleophillic aromatic substitutions (31-33). The potassium carbonate, hydroquinone and the 4,4´-dichlorobenzophenone (or difluorobenzophenone) were added to a 4 neck flask

equipped with a mechanical stirrer, thermometer, dean stark trap, nitrogen inlet and outlet, condenser and heating mantle. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of solvent. N-methylpyrrolidinone (NMP) and toluene were added via cannula. The reaction mixture was slowly heated to a stable reflux temperature of 180°C. The stoichiometry was such that a 10% excess of 4,4'-dichlorobenzophenone was present to control molecular weight. A temperature of 180°C was maintained until all of the water of reaction had been collected (7-10 hours). Additional 4,4'-dichlorobenzophenone in NMP was then added to ensure endcapping with chlorine. The reaction was continued for 2 hours. The reaction mixture was then cooled to room temperature and the polymer precipitated into acetone, washed with acetone and distilled water, and then dried under vacuum. The purified oligomer was then analyzed for chlorine to obtain an estimate of the number average molecular weight. The reaction was also run using 4,4'difluorobenzophenone. No difference in the polymerization, other than rate of reaction, was observed. In the second step, the oligomeric HDQPK and 10 times the stoichiometric amount of 1,4-phenylenediamine were placed into a 4 neck flask equipped as above. The stoichiometric amount was calculated using the assumption that the end groups and carbonyl groups were capable of reacting with the diamine. An amount of potassium carbonate equivalent to

one half the number of primary aromatic amine groups was also added. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of solvent. Toluene and NMP were added via cannula. The ratio of these two solvents was such that a stable reflux temperature of 190°C is obtained (NMP/toluene = 1/.1). Potassium carbonate must be used to accelerate the displacement of the chlorine end groups by the diamine. Stronger bases must be avoided to prevent water elimination from the hemiaminal groups at the carbonyls. The Schiff bases which would form cannot be removed easily. A temperature of 190°C is maintained for 8 hours. The amine-terminated oligomer is then precipitated into distilled water, washed with distilled water and dried. Elemental analysis for chlorine and nitrogen was carried out to estimate the amine termination efficiency and the percent of carbonyl groups which had been converted to hemiaminals. To remove the hemiaminals the polymer is suspended in a 10% solution of hydrochloric acid in distilled water. This suspension is refluxed for several hours. The polymer is again filtered, washed with distilled water and dried under vacuum. Elemental analysis for chlorine and nitrogen is repeated to insure that all of the hemiaminals have been removed. Termination of fluorine terminated HDQPK did not seem to occur any faster or produce any greater amine termination efficiencies than that obtained with the chlorine terminated HDQPK.

3.2.2 Resin Formulation

The functionalised oligomers were slowly added to the epoxy resins at temperatures as high as 280°C while mixing. Despite these high temperatures, the amine-terminated HDQPK did not dissolve into any of the epoxy resins tested. In the resin formulations which were cast into cured sheets, the amine-terminated HDQPK acted only as a filler, perhaps with a reactive surface forming covalent bonds with the epoxy matrix. In these cured resin formulations the amine-terminated HDQPK was added to the epoxy resin at 150°C while mixing. A 1/2 hour prereaction period was allowed followed by the addition of DDS . Mixing was continued for 5 minutes. At this point, upon cooling, the resin is in a B-stage. All formulations reported had sufficient tack and drape in this B-stage at room temperature for conventional prepreg lay up procedures. These formulations were made at an amine to epoxide ratio of 1.20. The DDS containing reaction mixtures were then degassed under vacuum at 180°C for 3 to 5 minutes and transferred to preheated aluminum sheet molds also at 180°C. These resins were cured for 2 hours at 180°C followed by 2 hours at 200°C under vacuum. The sheets were then allowed to cool slowly to room temperature to minimize thermal stresses. Compact tension and three point bend samples were cut from these sheets using a jewelers slotting blade on a Bridgeport milling

machine (appendix A). Precracks were inserted by a room temperature razor blade scoring technique (Appendix A). As a result of the dull, non reproducible precracks made from this precrack insertion technique, the fracture data cannot be compared to any of the data reported in any of the other chapters or to numbers reported in the literature. Therefore this data will not be reported numerically in this chapter. All formulations made with the amine-terminated HDQPK were equally or more brittle than the neat resin. No significant toughening effect was observed.

3.2.3 Mechanical Property Characterization

Critical stress intensity factors (K_{Ic}) and fracture energy (G_{Ic}) determinations were made on compact tension samples following a modified ASTM E399-83 procedure(21,22)(appendix B). Young's modulus calculations were performed in three point bend following ASTM D790M (appendix C). Both determinations were carried out on an Instron testing machine at a crosshead speed of .05cm/minute. Dynamic mechanical measurements were made on an IMASS Dynastat in three point bend (appendix D). Differential scanning calorimeter (DSC) measurements were made using a Perkin Elmer DSC II.

3.3 Results and Discussion

An aromatic amine-terminated HDQPK of 900 number average molecular weight and 66% amine termination was incorporated into Heloxy 69,and Epon 828 at various weight compositions (The diglycidyl ethers of resorcinol and bisphenol A obtained from Wilmington Chemical Company and Shell respectively). Table 3.1 summarizes the mechanical properties of these cured matrices. The amine-terminated HDQPK did not dissolve in Epon 828, Heloxy 69 or any of the other epoxy resins tested. The amine-terminated HDQPK remained particulate in the resin formulations. It can be expected that some covalent bonding occurred between the amine-functionalized HDQPK crystalline particles. All of the formulations investigated had sufficient tack and drape at room temperature for conventional prepreg lay up procedures. The amount of tack and drape decreased with increasing functionalised oligomer weight fraction. In Figures 3.2. and 3.3. the thermal behavior of the HDQPK and amine-terminated HDQPK is shown. These Differential Scanning Calorimetry scans show that the HDQPK at this molecular weight exhibits several melting peaks beginning at 240° C. The multiple melting peaks are probably a result of the presence of a distribution of molecular weight species. The bulk of the material melts between 280 and 300° C. The amine-terminated HDQPK exhibits a cold crystallization exotherm at 150° C, just above the glass transition

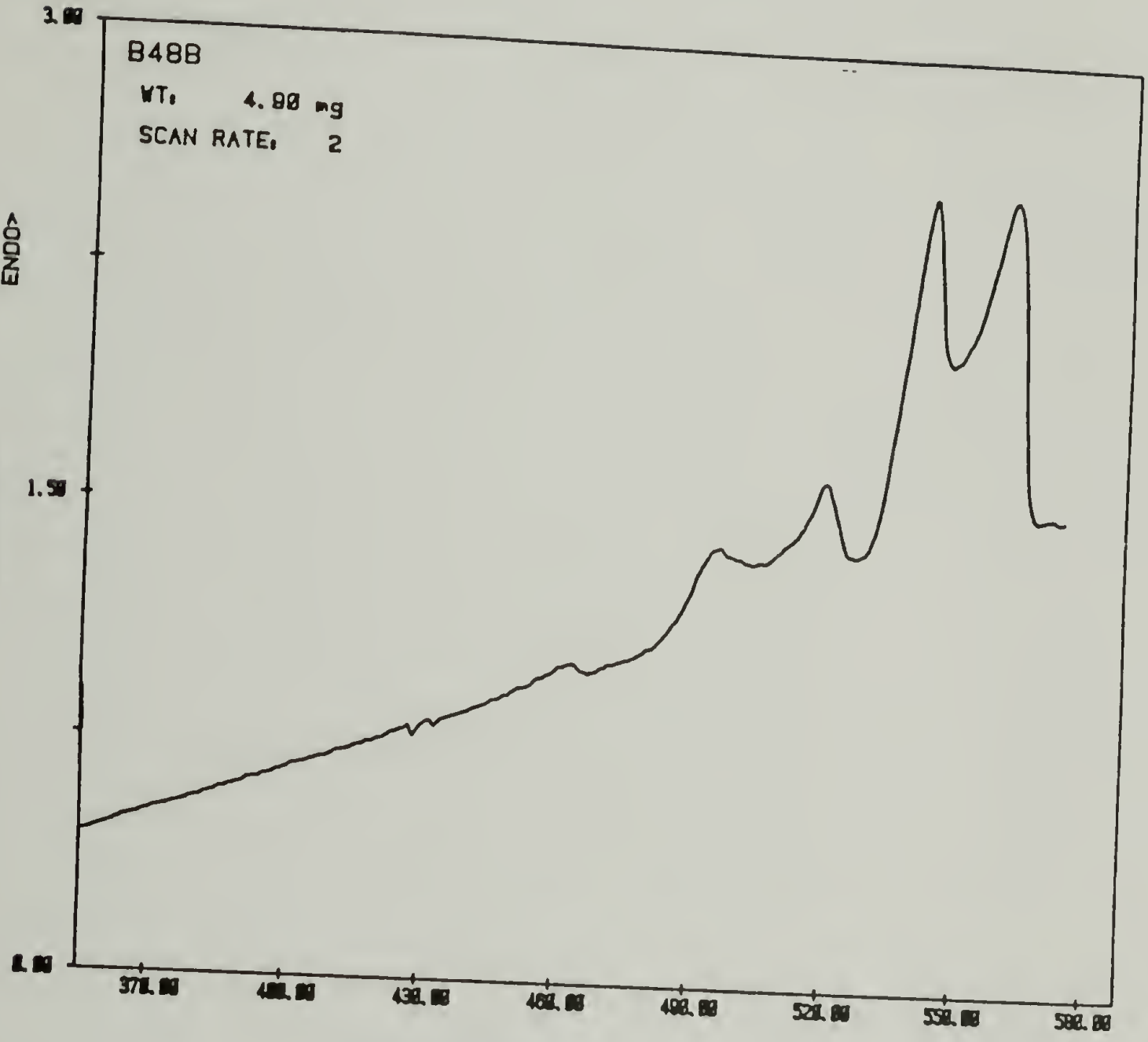


Figure 3.2 Differential Scanning Calorimeter scan for hydroquinone polyetheretherketone.

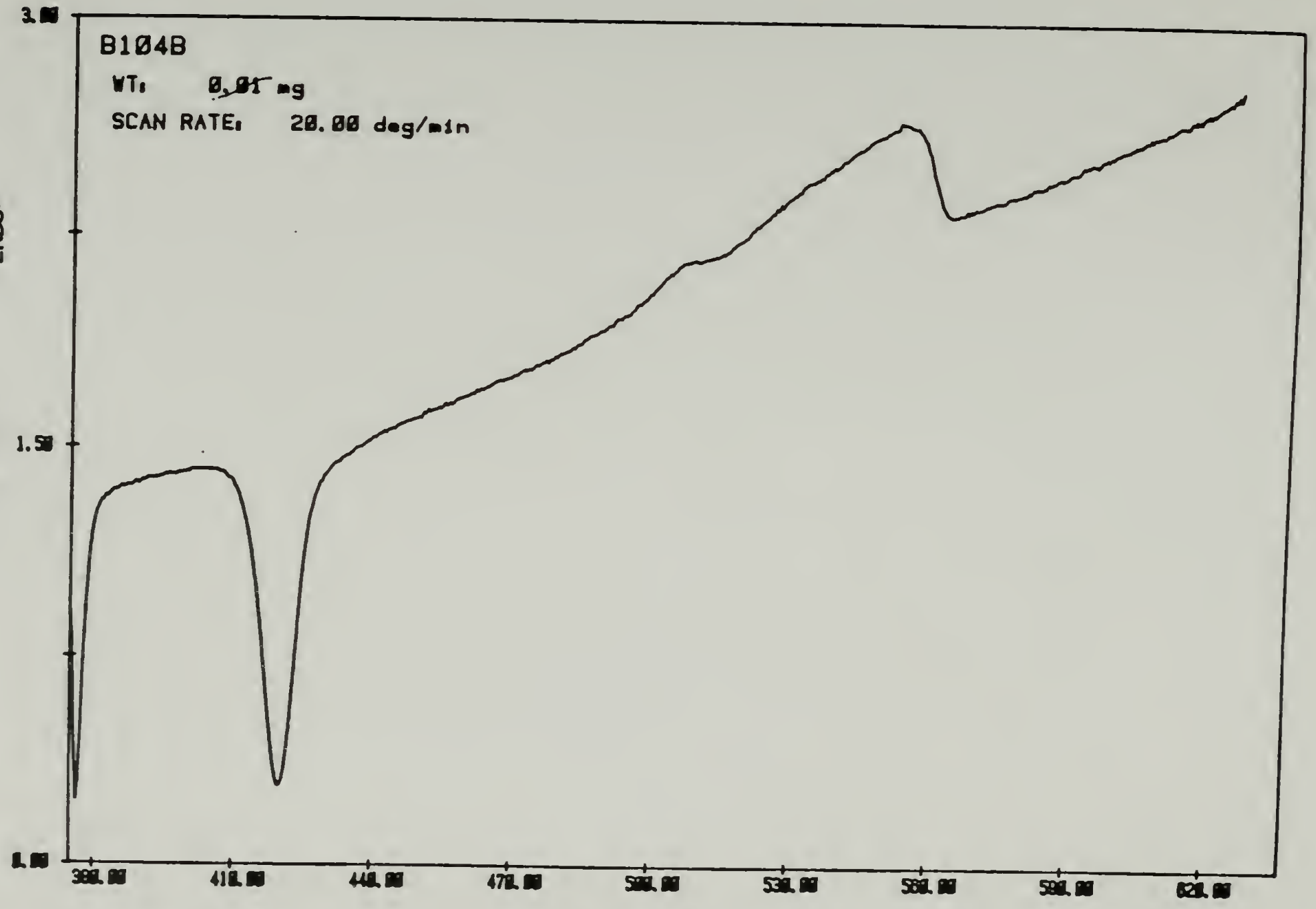


Figure 3.3 Differential Scanning Calorimeter scan for amine terminated hydroquinone polyetheretherketone.

temperature, and multiple melt transitions up to 300°C. The thermal behavior is not strongly affected by the presence of the aromatic amine end groups.

Figures 3.4.-3.7. are plots of the dynamic storage and loss moduli and loss tangent vs. temperature for the cured Heloxy 69 resin formulations. Figure 3.4. represents Heloxy 69 cured with DDS alone at an amine to epoxide ratio of 1.20. A glass transition temperature of 180°C is observed. Figures 3.5. to 3.7. represents the Heloxy 69/ DDS systems containing 20%, 35%, and 50% by weight HDQPK also at amine to epoxide ratios of 1.20. In these plots of the dynamic mechanical properties versus temperature glass transition temperatures of 160°c, 160°C, and 160°c are observed respectively. Some HDQPK obviously dissolved in the epoxy resin resulting in the observed lowering of the glass transition temperature. No effect of the weight percent of the functionalised oligomer added on the glass transition temperature is observed. As mentioned in the introduction, no significant changes in the fracture resistance of these resin formulations was observed. Since this work was carried out at an early stage in the Dissertation, (prior to the development of a suitable precrack insertion technique), the actual critical stress intensity and fracture energy values are not reported. Samples prepared using this poor insertion technique yielded precracks of varied sharpness as a result of the strong dependence of precrack sharpness on material stiffness and razor blade pressure therefore

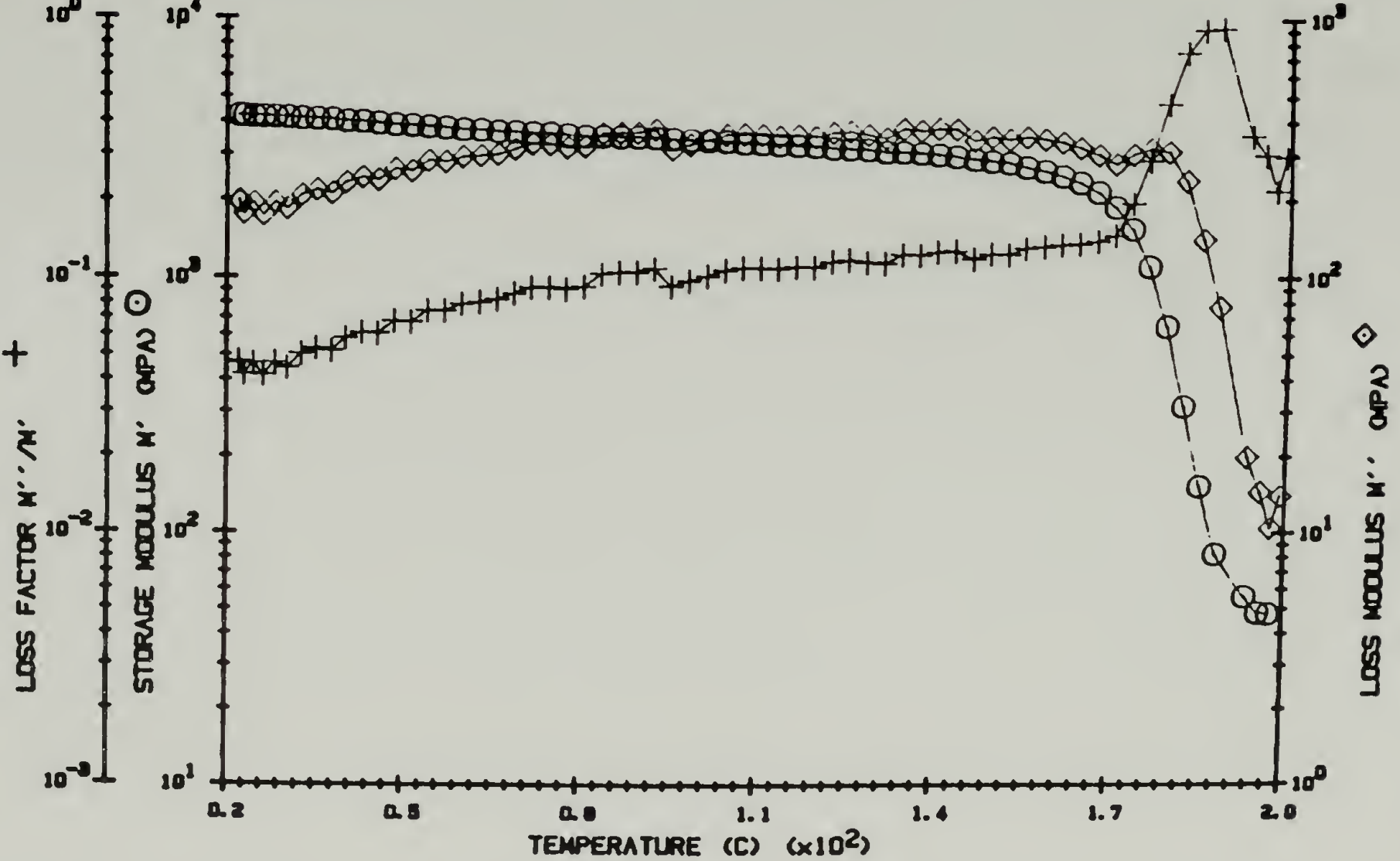


Figure 3.4 Dynamic Mechanical Properties of Heloxy 69/ DDS/ A/E = 1.2.

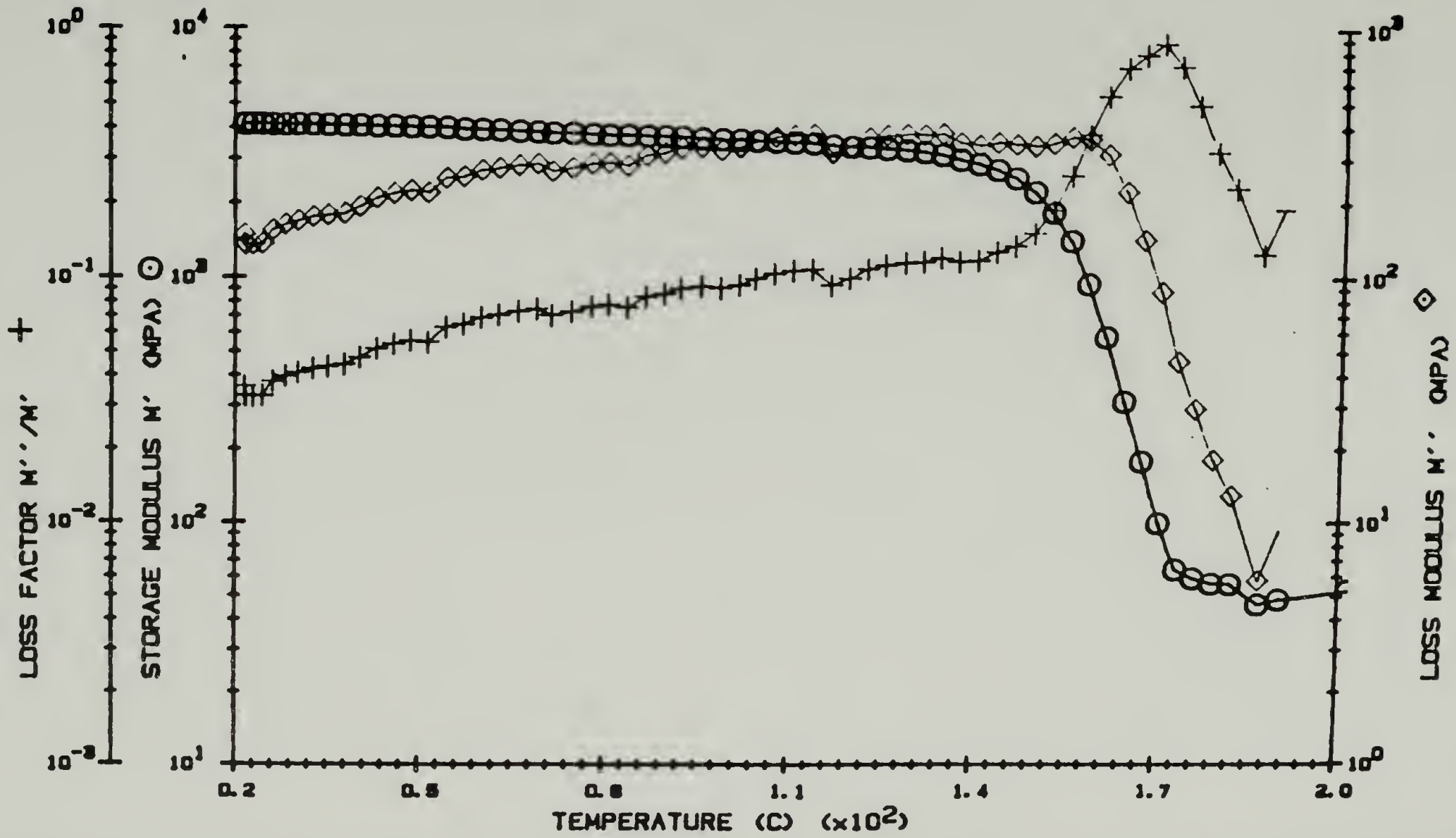


Figure 3.5 Dynamic Mechanical properties of Heloxy 69/ DDS/ 20% 900 Mn HDQPK/ A/E = 1.2.

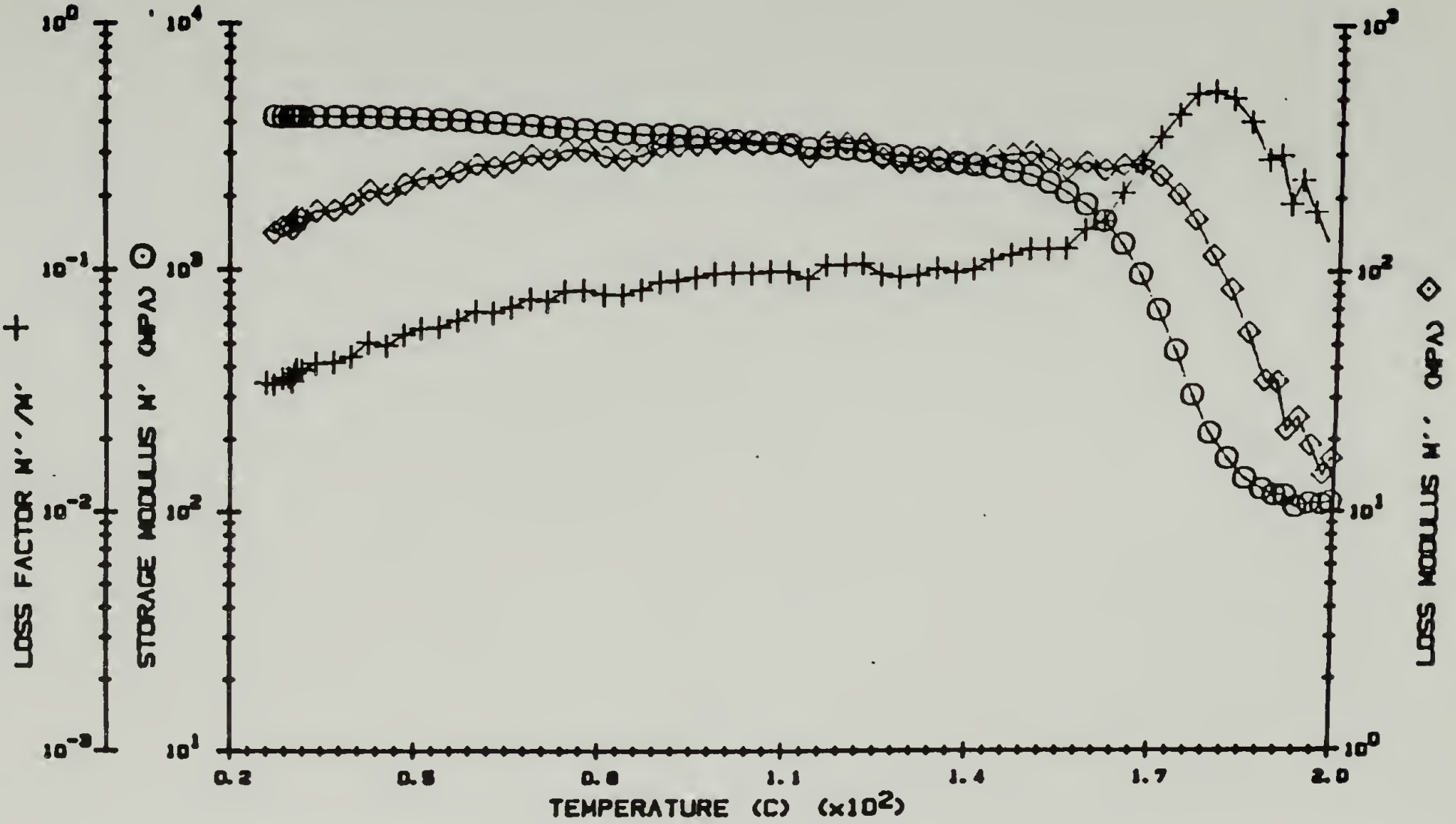


Figure 3.6 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 35% 900 Mn HDQPK/ A/E = 1.2.

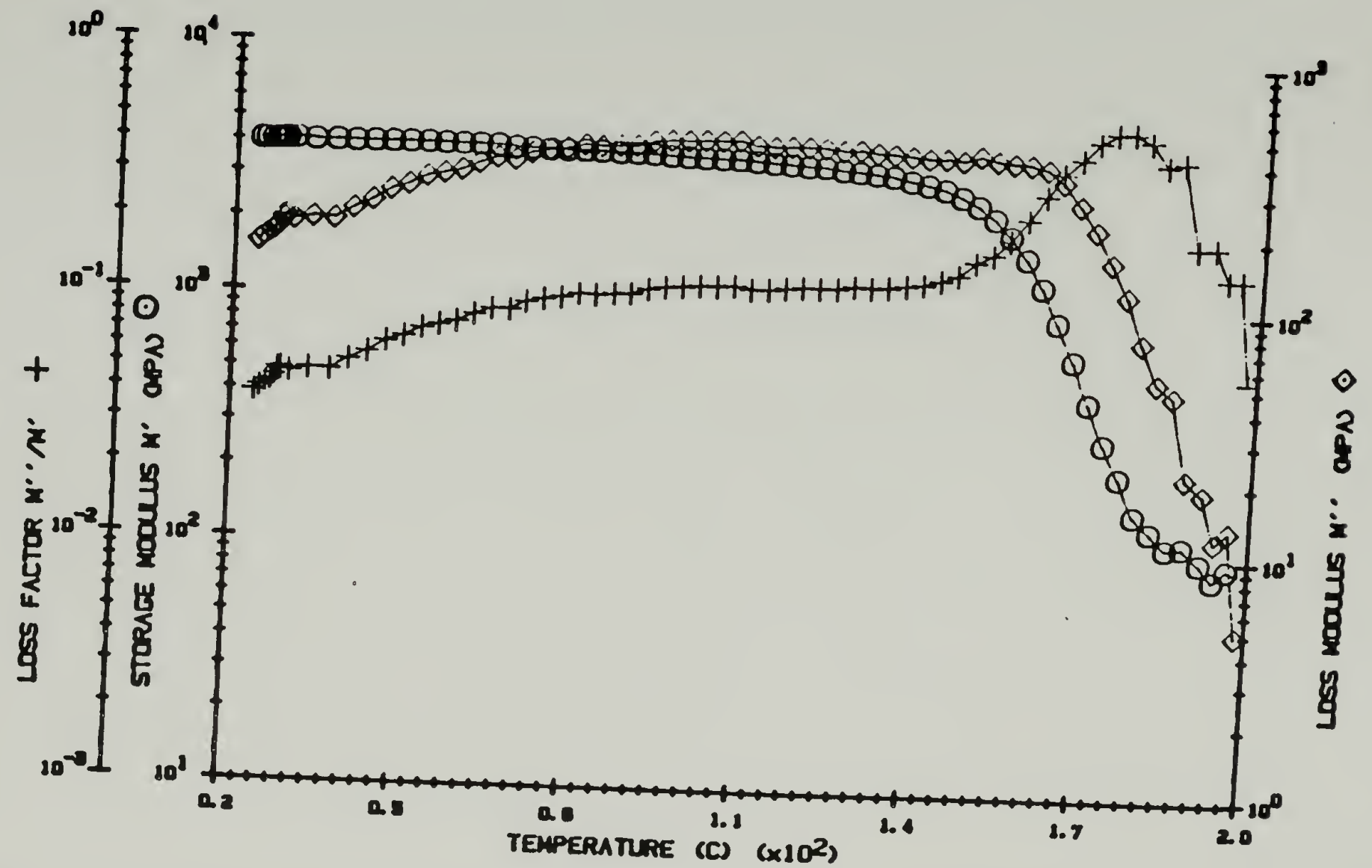


Figure 3.7 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 50% 900 Mn HDQPK/ A/E = 1.2.

leading to inaccurate data. The absolute numbers obviously cannot be compared to any of the other data obtained using the above Tg precrack insertion technique or to values in the literature. Qualitatively the resin formulations containing the amine-terminated HDQPK particles were less resistant to fracture than the neat resins.

3.4 Conclusions

Despite the success in the production of an amine-terminated HDQPK for use in conjunction with a commercial epoxy resin, this material was not soluble in any of the resins tested below 280° C. Therefore as a result of this insolubility and the inability of this material to toughen the epoxy network while in particulate form, it cannot be used in this type of application. No solvents other than strong acids could be found for this material at room temperature, precluding the use of a cosolvent for dispersal in the epoxy resin. Even if the material had produced a toughened resin formulation it would not have been suitable for use in composite applications as a result of the large particle size relative to the distance between fibers. As explained in the introduction to this dissertation, a material cannot be used in this type of application without solubility unless particle size can be kept below 3 to 5 microns. Unfortunately, particles which are in the desirable size range usually tend to aggregate during

processing and therefore cannot be used. It seems the only way to attain monodisperse particles of the correct size is through the process of phase separation under controlled conditions. Since a phase inverted morphology, having a HDQPK rich matrix was not possible, the solvent resistance characteristics of these amine-terminated HDQPK formulations would not be expected to differ from those of the neat resin and therefore were not investigated. Although this material could not be used for the desired high performance composite application it did lead to the development of a method for improving the high temperature performance of Victrex HDQPK which will be presented in chapter 7. The cause of the failure to develop a method for the incorporation of HDQPK into a commercial epoxy resin is undoubtedly the high melting crystalline nature of this polymer. The next natural step in the pursuit of a semicrystalline polyetheretherketone for incorporation into a commercial epoxy resin was to develop a lower melting polyetheretherketone. This step will be discussed in chapter 4.

Table 3.1
Resins Formulated Using a Hydroquinone Polyaryletherketone of Mn = 900 and an amine termination efficiency of >47%

Epoxy Resin	Percent Modifier	Amine	A/E	Tg °C	Young's Modulus
E828	0	DDS	1.2	175	3.45GPa
E828	20	DDS	1.2	160	3.78GPa
E828	35	DDS	1.2	160	3.54GPa
E828	50	DDS	1.2	160	3.45GPa

CHAPTER 4
METHYLHYDROQUINONE BASED POLYARYLETHERKETONE AS A MATRIX MODIFIER WITH COMMERCIAL EPOXY RESINS

4.1 Introduction

Despite the failure encountered with the amine terminated HDQPK the idea of a phase separated matrix material containing a semicrystalline phase was still attractive. The next obvious step was to synthesize a semicrystalline polyetheretherketone having a low enough melt temperature such that dissolution in a common solvent at a low temperature was possible. Solubility in a common solvent below 135°C would allow for the use of the amine termination reaction used on BPAPK. A lower melting point would also facilitate dissolution into an epoxy resin at a reasonable temperature. It is well known that the introduction of side groups to semicrystalline polymers results in a reduction in the perfection of the crystal structure (45,46). This reduction in crystal perfection is usually accompanied with a decrease in the crystal melt temperature. Since methylhydroquinone is an inexpensive, commercially available material with a reactivity similar to that of hydroquinone, it was chosen to produce the next polyetheretherketone for investigation.

Methylhydroquinone polyetheretherketone (MeHDQPK) is indeed a semicrystalline polymer having a glass transition temperature of 145°C and a crystalline melting temperature of 240°C, 85°C below that of HDQPK. The structure of this polymer is illustrated in Figure 4.1.. In Figure 4.2. a differential scanning calorimeter scan of MeHDQPK is shown. No work involving the amine functionalisation or use of this polymer in an epoxy resin formulation has been reported. This polymer is readily soluble in an NMP / toluene mixture below 100°C and is quite suitable for amine termination via the technique used on the BPAPK without the problem of reverse attack or hemiaminal formation. It was also discovered that this polymer in the primary aromatic amine terminated form dissolves readily into Epon 828 at it's melting temperature (240°C).

4.2 Experimental

Potassium carbonate, potassium hydroxide, methylhydroquinone, 4,4'-difluorobenzophenone, 4-aminophenol, and diaminodiphenylsulphone (DDS) were obtained from Aldrich Chemical Company in the highest purity available. Epon 828 was obtained from Shell Chemical Company. N-methylpyrrolidinone was vacuum distilled from P_2O_5 and stored under nitrogen. Toluene was distilled from CaH_2 and stored under nitrogen.

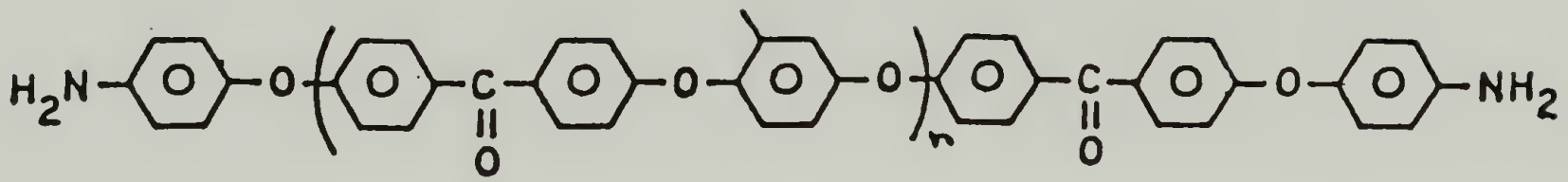


Figure 4.1
METHYLHYDROQUINONE POLYETHERETHERKETONE

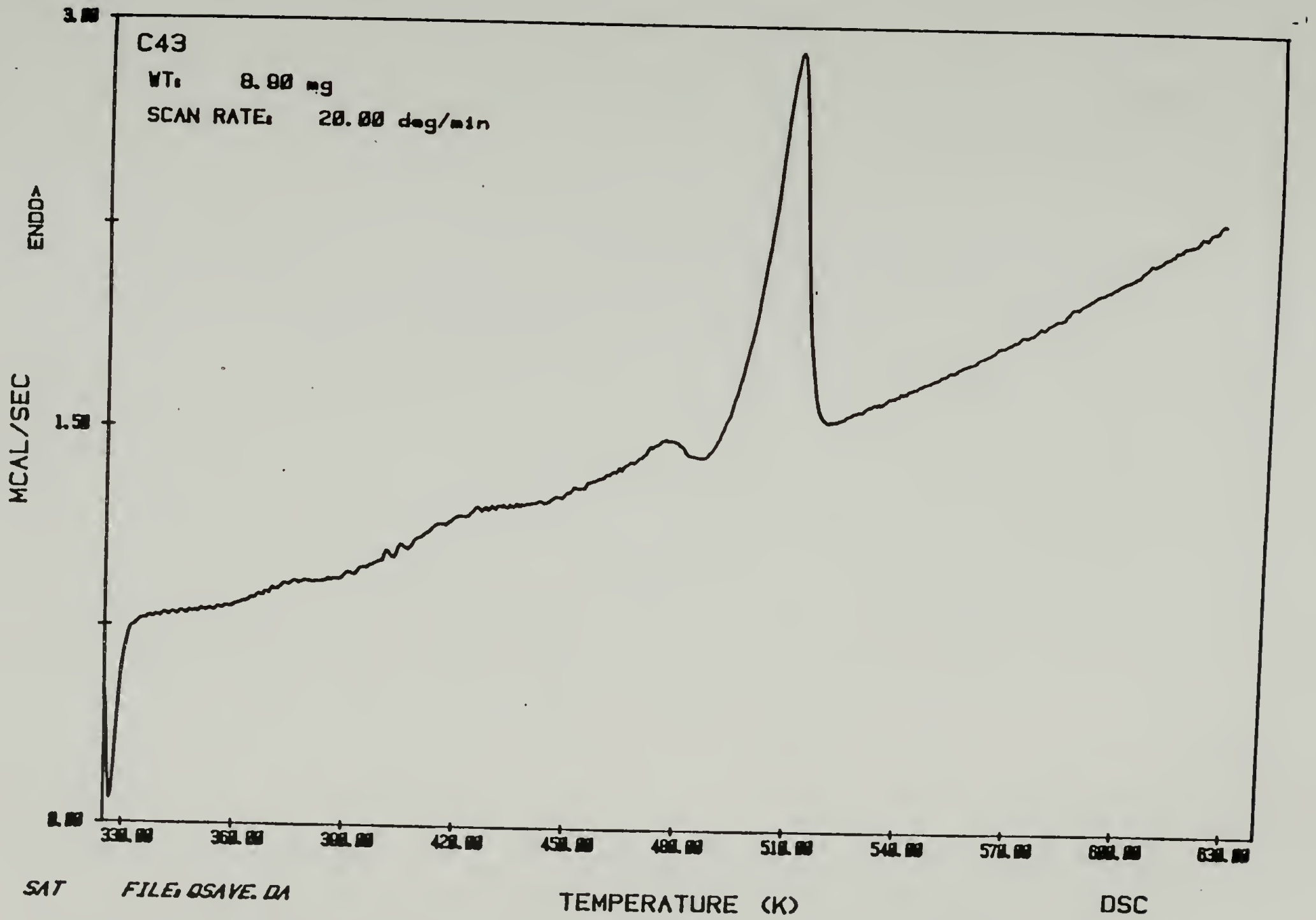


Figure 4.2 Differential Scanning Calorimeter scan of Methylhydroquinone polyetheretherketone.

4.2.1 Synthesis of Oligomeric Aromatic Amine Terminated Polyaryletherketone

Both the polymerization and endcapping reactions are nucleophillic aromatic substitutions (31-33). The potassium carbonate, methylhydroquinone, and the 4,4′-difluorobenzophenone were added to a 4 neck flask equipped with a mechanical stirrer, thermometer, dean stark trap, nitrogen inlet and outlet, condenser and heating mantle. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of solvents. N-methylpyrrolidinone (NMP) and toluene were added via cannula. The reaction mixture was slowly heated to a stable reflux temperature of 160°C. The stoichiometry was such that a 5-10% excess of 4,4′-difluorobenzophenone was present to control molecular weight. A temperature of 160°C was maintained until all of the water of reaction had been collected (3-4 hours). Additional 4,4′-difluorobenzophenone in NMP was then added to ensure endcapping with fluorine. The reaction was continued for 1 hour after which toluene was removed quantitatively from the reaction flask. The reaction mixture was then cooled to room temperature and the polymer precipitated into methanol, washed with methanol, and distilled water, then dried under vacuum. The purified oligomer was then analyzed for fluorine (appendix F) to obtain an estimate of the number average molecular weight.

In the second step the oligomeric methylhydroquinone polyetheretherketone (MEHDQPK) and a stoichiometric amount of 4-aminophenol were placed into a 4 neck flask equipped as above. The flask was continuously purged with nitrogen starting 20 minutes prior to the addition of solvent. Toluene and NMP were added via cannula. The ratio of these two solvents is such that a stable reflux temperature of 135° C is obtained (NMP/toluene = 1/1). It is important to keep the temperature as low as possible to prevent significant attack by the amine group (34). It also seems important to keep the reaction flask free of oxygen to prevent oxidation of the 4-aminophenol. When the reaction mixture reaches 100° C a stoichiometric amount of oxygen free 50% potassium hydroxide in water is added via cannula. An excess of base must be avoided to prevent attack by the amine at the fluorine end groups and/or attack at the carbonyls (35). A temperature of 135° C is maintained until all of the water of reaction has been collected (1.5-2 hrs). Most of the toluene is then removed from the reaction mixture through the dean stark trap. The amount of toluene removed is measured by the reflux temperature. At a reflux temperature above 170° C, enough toluene has been removed to allow the polymer to precipitate in the purification solvent. If enough toluene is not removed the polymer forms a toluene swollen mass which cannot be easily purified. During toluene removal the time above 135° C should be kept

to a minimum to prevent hemiaminal formation. After completion of toluene removal the reaction mixture is quenched to room temperature. The amine terminated oligomer is then precipitated into methanol, washed with methanol, resuspended in hot distilled water, washed with distilled water and dried under vacuum at 90°C. Elemental analysis for fluorine is again carried out to estimate the amine termination efficiency. A non-aqueous amine titration is also performed to confirm the amine termination efficiency (appendix F).

4.2.2 Resin Formulation

The functionalized oligomers were slowly added to the epoxy resins at room temperature while mixing. The mixture was then placed in a vacuum oven at 240°C under reduced pressure. Approximately 10 to 20 minutes at 240°C was required for complete melting and dissolution into the Epon 828. The beaker containing the reaction mixture was then immersed in an oil bath at 150°C. The beaker and contents were allowed 5 to 10 minutes to reach temperature equilibration during which the reaction mixture was mixed vigorously. The DDS was then added. Mixing was continued for 5 minutes. At this point, upon cooling, the resin is in a B-stage. All formulations reported had sufficient tack and drape in this B-stage at room temperature for

conventional prepreg lay up procedures. These formulations were made at an amine to epoxide ration of 1.0. The DDS containing reaction mixtures were then degassed under vacuum at 180°C for 3 to 5 minutes and transferred to preheated aluminum sheet molds, also at 180°C. These resins were cured for 2 hours at 180°C followed by 2 hours at 200°C under vacuum. The sheets were then allowed to cool slowly to room temperature to minimize thermal stresses. Compact tension and three point bend samples were cut from these sheets using a jewelers slotting blade on a Bridgeport milling machine (appendix A). Precracks were inserted by an above Tg insertion technique(36)(appendix A).

4.2.3 Mechanical Property Characterization

Critical stress intensity factors (K_{Ic}) and fracture energy (G_{Ic}) determinations were made on compact tension samples following a modified ASTM E399-83 procedure(37-39) (appendix B). The fracture data reported may not be true K_{Ic} and G_{Ic} values as a result of the thin compact tension samples used and the uncertainty of the satisfaction of the plain strain condition assumed in the derivation of the ASTM E399 equations. Due to the very small amounts of material available for testing, an investigation into the effect of thickness could not be carried out. The fracture surfaces did not suggest plane stress conditions nor was their

significant plastic deformation prior to the initiation of crack growth since Pmax/P_Q is $\leq$ 1.0. Pmax and P_Q are as defined in ASTM E399.

Young's modulus calculations were performed in three point bend following ASTM D790M (appendix C). Both determinations were carried out on an Instron testing machine at a crosshead speed of .05cm/minute. Dynamic mechanical measurements were made on an IMASS Dynastat in three point bend (appendix D). Differential scanning calorimeter (DSC) measurements were made using a Perkin Elmer DSC II.

4.3 Results and Discussion

An aromatic amine terminated MeHDQPK of 5,300 number average molecular weight and 93% amine termination was incorporated into Epon 828 at various weight compositions. Table 4.1 summarizes the mechanical properties of these cured matrices. For standard deviation data see appendix G. Phase separation was visibly evident in all of the cured materials. In the Epon 828 formulations the cured resins were opaque suggesting phase separation into domains of sizes on the order of the wavelength of visible light. Since phase separation and gelation are thermodynamic and kinetic processes, the Epon 828 resin must have a combination of solubility parameter, viscosity behavior and

TABLE 4.1 MECHANICAL DATA

RESINS FORMULATED USING A METHYLHYDROQUINONE PEEK OF Mn = 5,000 AND AN AMINE TERMINATION EFFICIENCY OF > 93%

EPOXY RESIN	PERCENT MODIFIER	YOUNG'S MODULUS	K_{Ic} $N/M^{3/2}$	G_{Ic} J/M^2	Tg ^oC	PHASE SEP.
E828	0	2.52GPa	$.89x10^6$	315	200	No
E828	10%	2.57	$.91x10^6$	319	195	Micro
E828	20%	2.96	$1.0x10^6$	359	195	Micro
E828	30%	---	$.97x10^6$	403	195	Micro

cure kinetics which provides for this small domain size. For composite use, where inter fiber spacing is approximately 3 to 5 microns these Epon 828 formulations would be suitable. All of the formulations investigated had sufficient tack and drape at room temperature for conventional prepreg lay up procedures. The amount of tack and drape decreased with increasing functionalized oligomer weight fraction. The loading limit set by the presence of tack and drape at room temperature in the B-stage was 30% for this 5,300 Mn MeHDQPK. In the Epon 828 resins it was discovered that K_{Ic}, and G_{Ic} increased slightly with the weight percent of the aromatic amine terminated MeHDQPK added. Figure 4.3. is a plot of K_{Ic} vs. weight concentration of the functionalized oligomer for these Epon 828 formulations. Increases in the K_{Ic} value of 14% and 26% were obtained for the 20 and 30% loading levels. As a result of the overlap in the standard deviations of these K_{Ic} values these increases are not significant. In fact the highest increase in K_{Ic} was observed in a sample having a 20% loading of particulate amine terminated MeHDQPK which was processed at a temperature below that of the MeHDQPK melt temperature. In Figure 4.4 G_{Ic} versus the weight concentration of the functionalized oligomer is shown. For these resin formulations an increase in Young's modulus of 17% was obtained at the 20 percent loading level. A Young's modulus value could not be obtained for the 30% loading

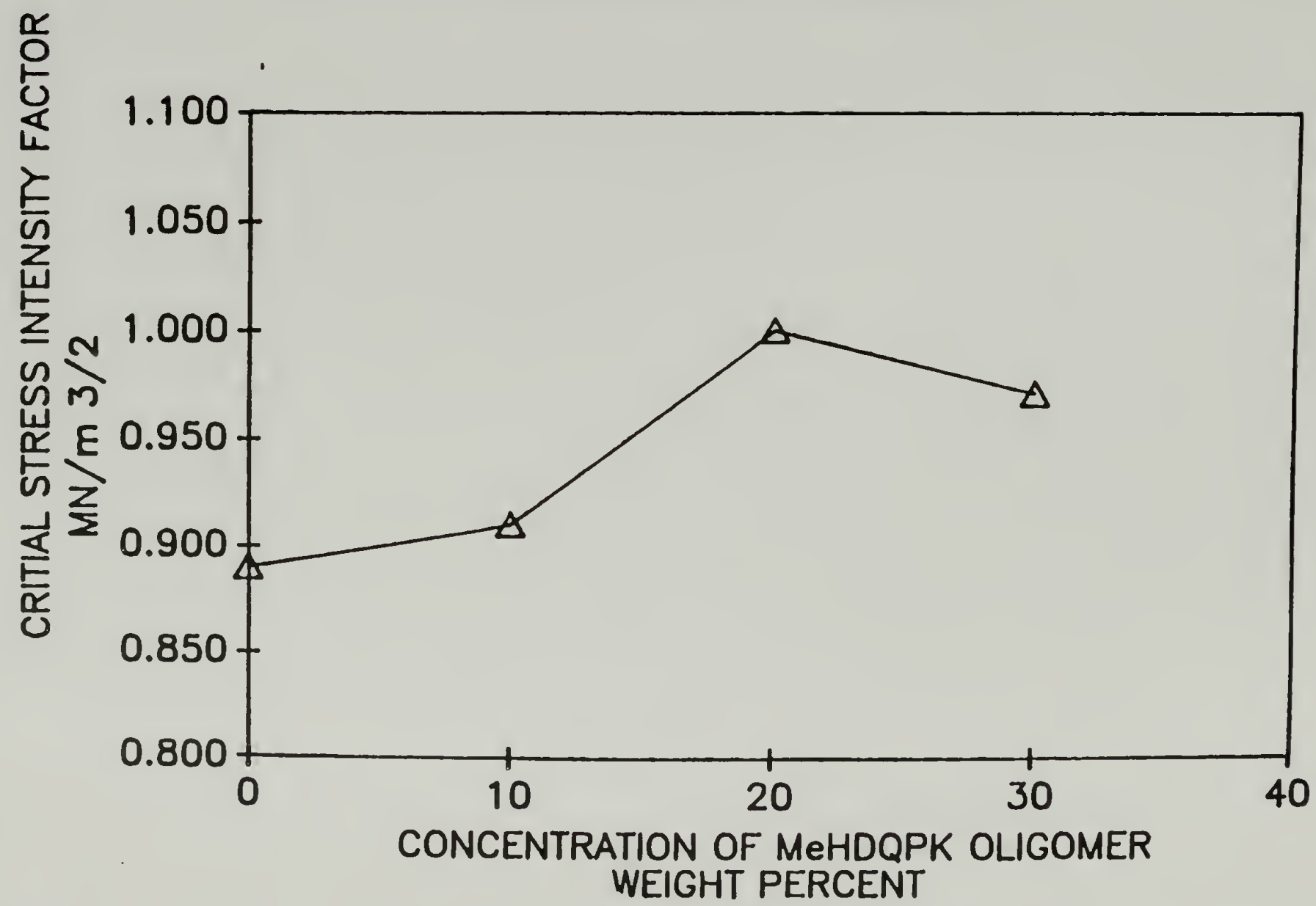


Figure 4.3 Critical Stress Intensity Factor vs. Concentration of MEHDQPK in Epon 828.

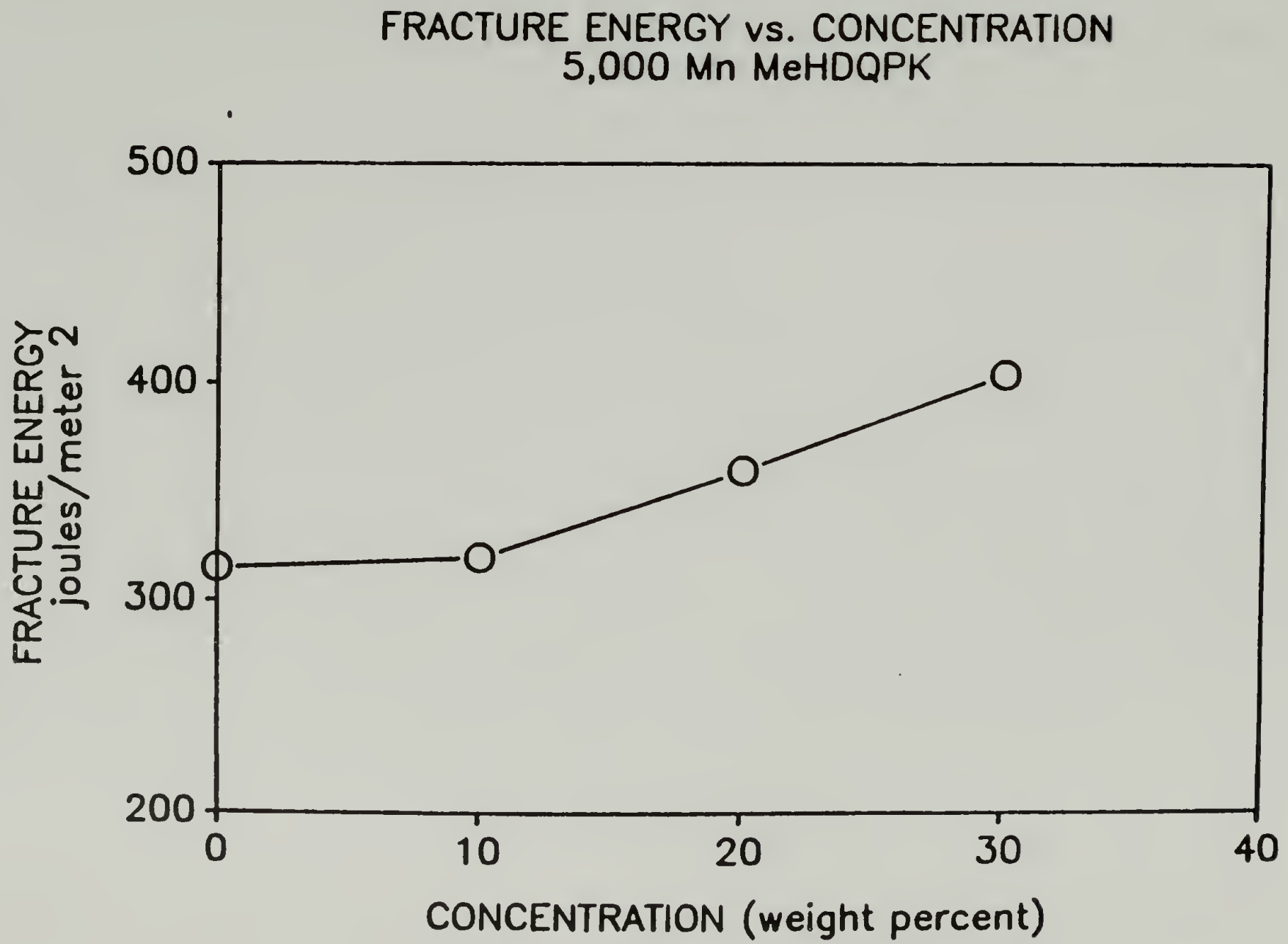


Figure 4.4 Fracture Energy vs. Concentration of MEHDQPK in Epon 828.

level as a result of insufficient sample size for three point bend determination. Figures 4.5.-4.7. are plots of the dynamic storage and loss moduli and loss tangent vs. temperature for the cured resin formulations. Despite the phase separation, only one glass transition is seen in each of the cured modified resins. At this low molecular weight the phase separation is probably not complete leading to appreciable amounts of MeHDQPK in each phase. Under these circumstances it is not unlikely that the two phases have similar glass transition temperatures which cannot be distinguished. This factor in combination with the tremendous drop in material stiffness at the first transition temperature and the inherent lack of sensitivity of the Dynastat on three point bend samples of this thickness results in the measurement of only one glass transition temperature. From the dynamic mechanical data it was observed that the glass transition temperature decreased upon the addition of this oligomer, however remained constant at 195° C with increasing weight percent addition. The glass transition temperature was lower in the resin processed below the melt temperature of the MeHDQPK. This information is tabulated in Table 1..

In figure 4.8. the differential scanning calorimeter data for the Epon 828/ DDS resin formulation containing 30% MeHDQPK by weight is shown. No melt transition is observed in this DSC scan. Therefore the original motivation for

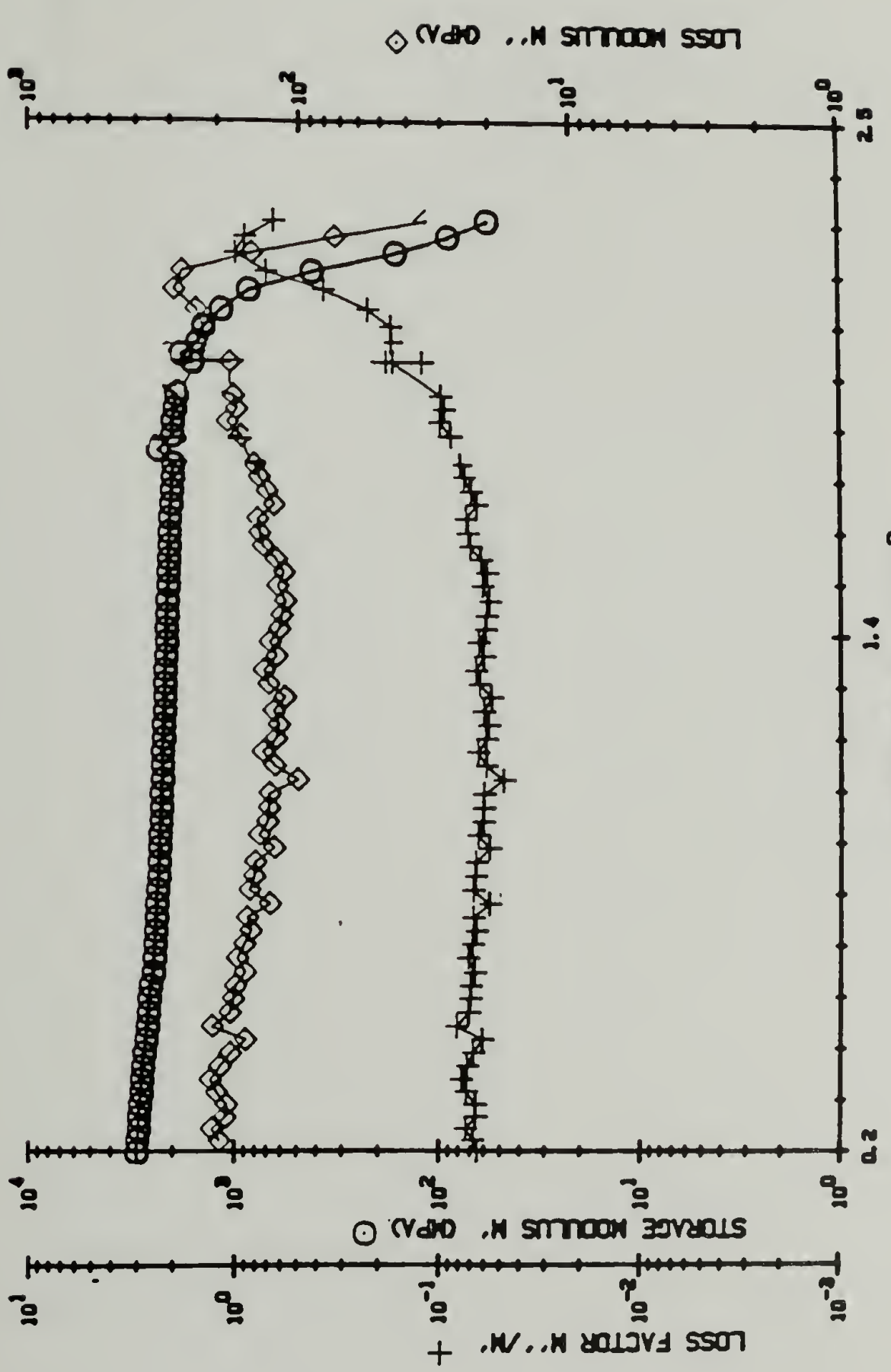


Figure 4.5 Dynamic Mechanical Properties of Epon 828/ DDS/ A/E = 1.0

Figure 4.6 Dynamic Mechanical Properties of Epon 828/ DDS/ 10% 5,000 Mn MEHDQPK/ A/E = 1.0.

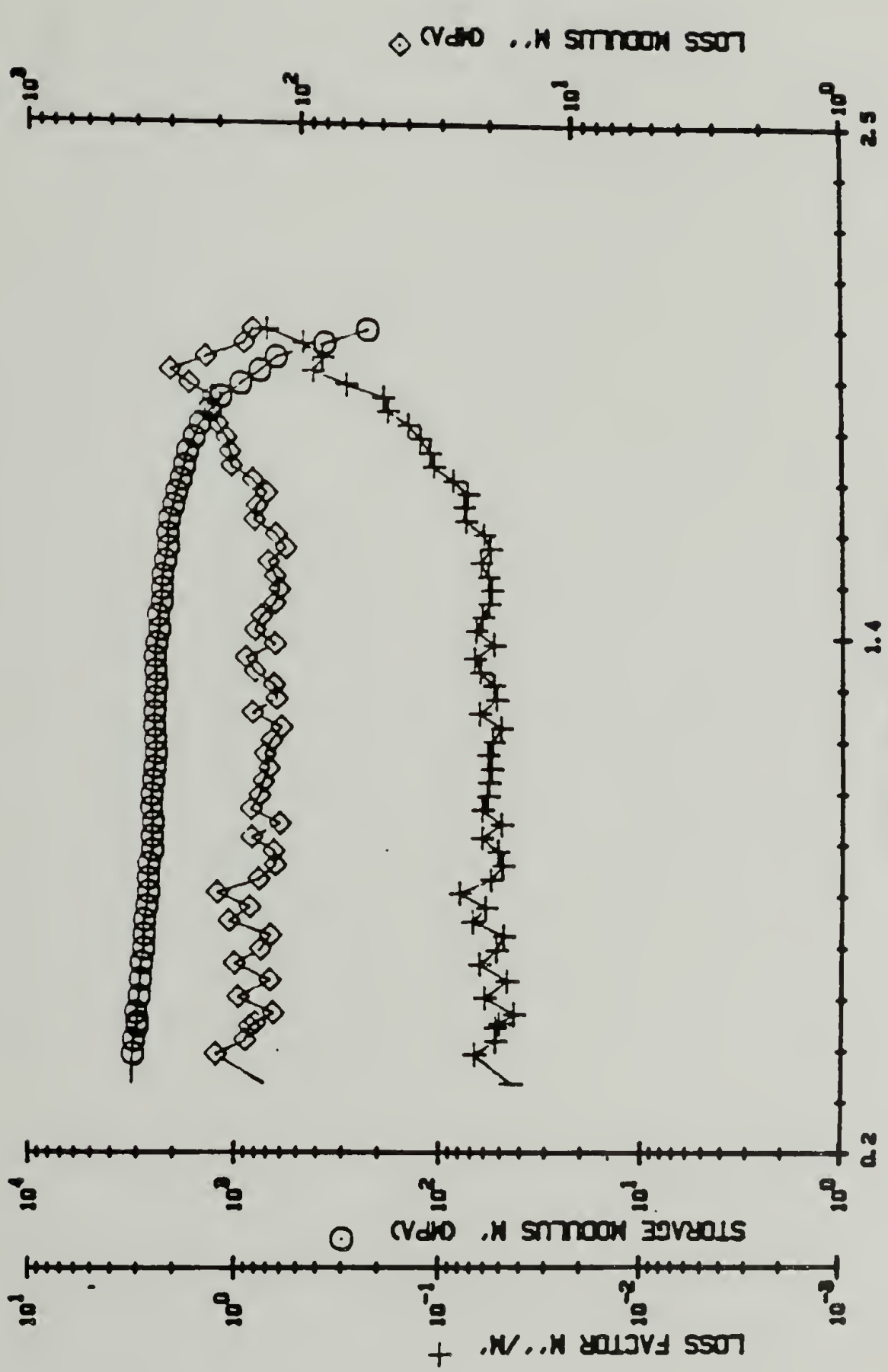


Figure 4.7 Dynamic Mechanical Properties of Epon 828/ DDS/ 20% 5,000 Mn MEHDQPK/ A/E = 1.0.

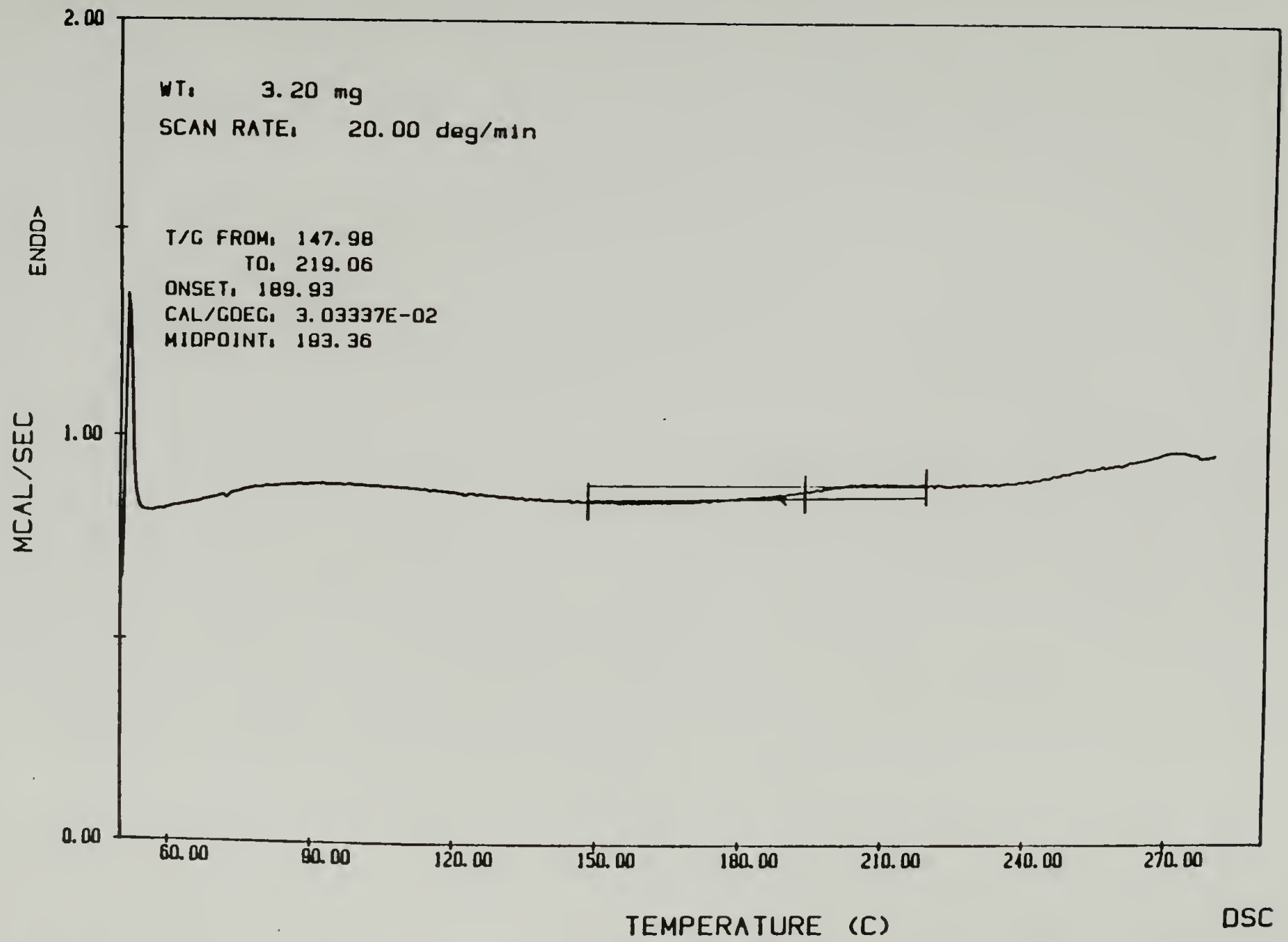


Figure 4.8 Differential Scanning Calorimeter scan of melt processed Epon 828/ DDS/ 30% 5,000 Mn MEHDQPK/ A/E = 1.0.

using the semicrystalline polyetheretherketone has not been realized. The material did not form a crystalline morphology in the MeHDQPK rich regions. In Figure 4.9. a DSC scan of a resin formulation containing 30% by weight undissolved MeHDQPK which was processed at 160°C, 80°C below the melting temperature of the MeHDQPK is shown. Surprisingly this scan shows no melt transition either! The exposure to the epoxy resin, while not dissolving the MeHDQPK particles, did result in the melting of the crystals at a temperature far below their original melting temperature.

4.4 Conclusions

A tough matrix material cannot be achieved via the incorporation of an oligomeric end functionalized methylhydroquinone polyetheretherketone into a commercial epoxy resin. Higher molecular weight functionalized oligomers may yield higher K_{Ic} values however as a result of the high viscosities encountered at the 5,300 number average molecular weight level higher molecular weight oligomers would not be processable. The high processing viscosities observed are probably a result of homopolymerization of the epoxy resin at the 240°C oligomer incorporation temperature (8). This homopolymerization would lead to a higher molecular weight, slightly crosslinked resin formulation

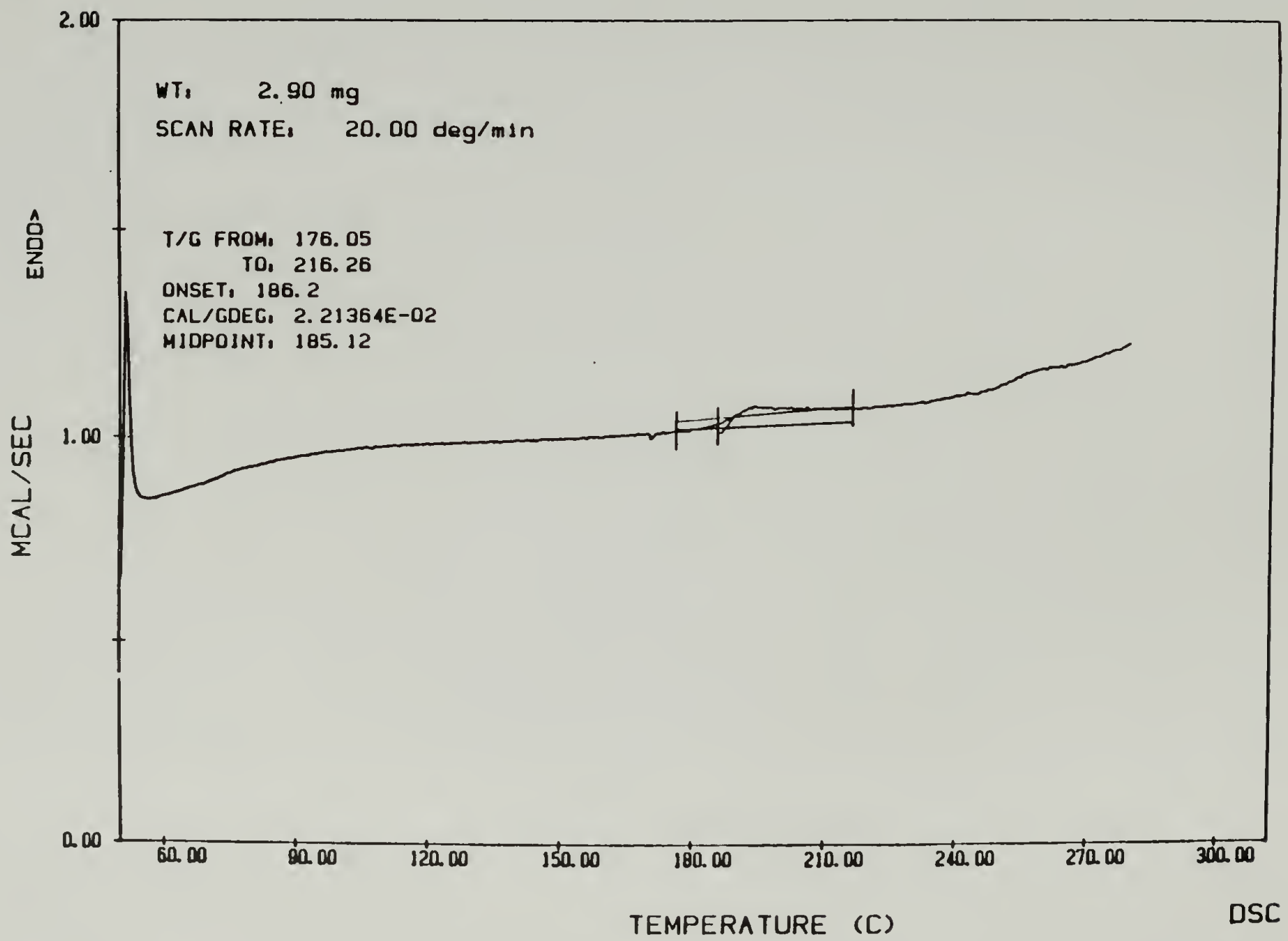


Figure 4.9 Differential Scanning Calorimeter scan of Epon 828/ DDS/ 30% 5,000 Mn MEHDQPK/ A/E = 1.0 processed below Tm.

with increased viscosity at a given temperature. The presence of trace amounts of base in the amine terminated MeHDQPK oligomer constituent may have accelerated this reaction (8). The solution to this problem of homopolymerization lies in the development of a lower melting semicrystalline material of high purity. In chapter 5 the development of such a material is investigated. The insubstantial increase in resistance to fracture makes these materials unattractive for composite use. Since crystals having a 240°C melting temperature could not remain stable in the epoxy resin at 160°C it is unlikely that a lower melting polymer would develop any crystallinity in these systems. Phase separation would have to be near 100% to prevent crystal disruption by the epoxy. If a higher molecular weight MeHDQPK could have been used, forcing more complete phase separation, perhaps crystallinity would have developed in the MeHDQPK rich regions. This crystallinity would lead to improved solvent resistance of the matrix material. Since crystallinity did not develop, solvent resistance was not investigated. With respect to the phase separation process, it is thought that these materials behave similarly to the amine terminated polyethersulphone (ATPEES) systems where at low percent incorporations the phase separated morphology consists of an epoxy matrix with ATPEES rich inclusions and at high percent incorporations the matrix is ATPEES rich and the inclusions are epoxy rich

(23-26). In the MeHDQ system at the lower loading levels the cured resin should consist of MeHDQPK rich inclusions in an epoxy/curing agent rich matrix. In this situation the MeHDQ rich inclusions should act as stress concentrators in the matrix. These stress concentrations should be very small as a result of the similarity in tensile, shear and bulk moduli of the two phases. These stress concentrations may cause the initiation of localized shear yielding in the matrix resulting in small increases in the resistance to crack propagation. These inclusions should also have the ability to deform in a ductile manner thereby increasing the energy required for crack propagation further. Increases in fracture resistance were not observed. The reasons for this are obscure. At the higher loading level it is expected that there is a phase inversion in which the inclusions are now epoxy/curing agent rich and the matrix is MeHDQPK rich. In this morphology the distance between crosslinks in the matrix is greatly increased allowing for the chain mobility required for large energy absorbing deformations. Therefore at these high loading levels the inherent level of ductility of the material should be greatly increased. Again no significant increases in energy absorption were observed. Perhaps the MeHDQPK polymer is itself a brittle material. Since a sufficiently high molecular weight MeHDQPK was not synthesized the homopolymer mechanical behavior could not be investigated.

Although the attempt to use this polymer in a tough, processable, matrix resin formulation failed, this attempt did elucidate two important facts. The first was the revelation that process temperatures must be kept low to avoid epoxide homopolymerization. The second was only recently realized after reading a journal article by McGrath et. al. dealing with the synthesis of an amorphous hydroquinone / tertiarybutylhydroquinone polyetheretherketone (47). The motivation for this synthesis was to avoid crystal formation during synthesis, allowing the use of NMP at 200° C instead of diphenyl sulphone at 270° C. This solvent change reduced the difficulties encountered in polymer purification as well as process temperatures. McGrath subsequently removed the tertiarybutyl groups to yield semicrystalline HDQPK. It is apparent that this is a labor intensive process, requiring two steps instead of one. Since the applications of HDQPK are limited severely by it's Tg of 143° C, and not significantly dependent upon the crystalline melting temperature (48) it seems much more reasonable to use MeHDQPK. As pointed out earlier MeHDQPK is also semicrystalline, having a Tg of 145° C and a melting temperature of 240° C. This polymer is already soluble in NMP below 100° C! No dealkylation step is necessary. It can also be melt processed 85° C below the temperature at which

HDQPK can be processed. Therefore MeHDQPK may be a more processable alternative to HDQPK that has not yet been investigated.

In conclusion, while the ability of this technique for improving the mechanical properties of matrix resins with amorphous aromatic chain oligomers has been clearly documented, until now there has been no published information on the use of a semicrystalline oligomer to produce formulations which are processable via conventional methods.

CHAPTER 5

TERTIARY-BUTYLHYDROQUINONE BASED POLYARYLETHERKETONE AS A MATRIX MODIFIER WITH COMMERCIAL EPOXY RESINS

5.1 Introduction

In the pursuit of a semicrystalline polyetheretherketone which would lend itself readily to incorporation into an epoxy resin at a temperature where homopolymerisation of the epoxide groups is not a problem, a bulkier side group was sought. This bulky group had to be larger than a methyl group to disrupt crystal perfection more than that found with the MeHDQPK. Since tertiarybutylhydroquinone is inexpensive and commercially available, it was the monomer of choice.

The structure of tertiarybutylhydroquinone polyetheretherketone (tBUHDQPK) is shown in Figure 5.1.. A DSC scan of this material is illustrated in Figure 5.2. Unfortunately tBUHDQPK is an amorphous polymer having a glass transition temperature of 145°C. The tertiarybutyl group was too large to accommodate crystal formation in the polymer. In retrospect a MeHDQ / tBUHDQ polyetheretherketone copolymer may have had the low melting semicrystalline nature that was desired. As a result of it's amorphous nature, tBUHDQPK is as easy to work with as the BPAPK, and in fact yielded resin formulations with

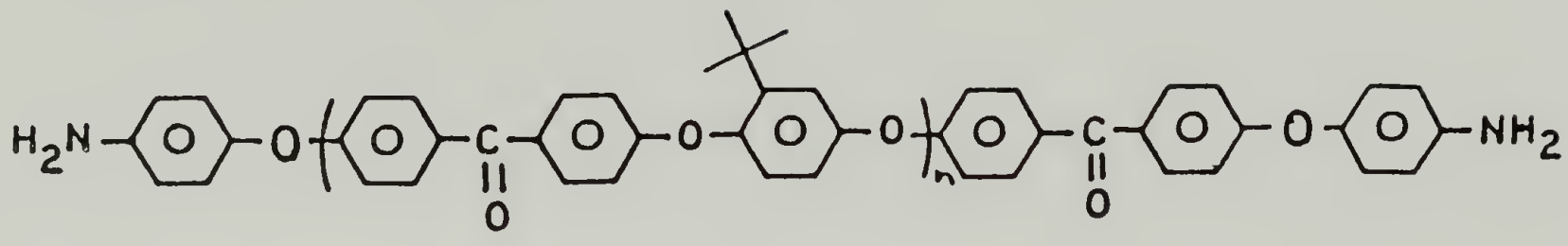


Figura 5.1
TERTIARYBUTYLHYDROQUINONE POLYETHERETHERKETONE

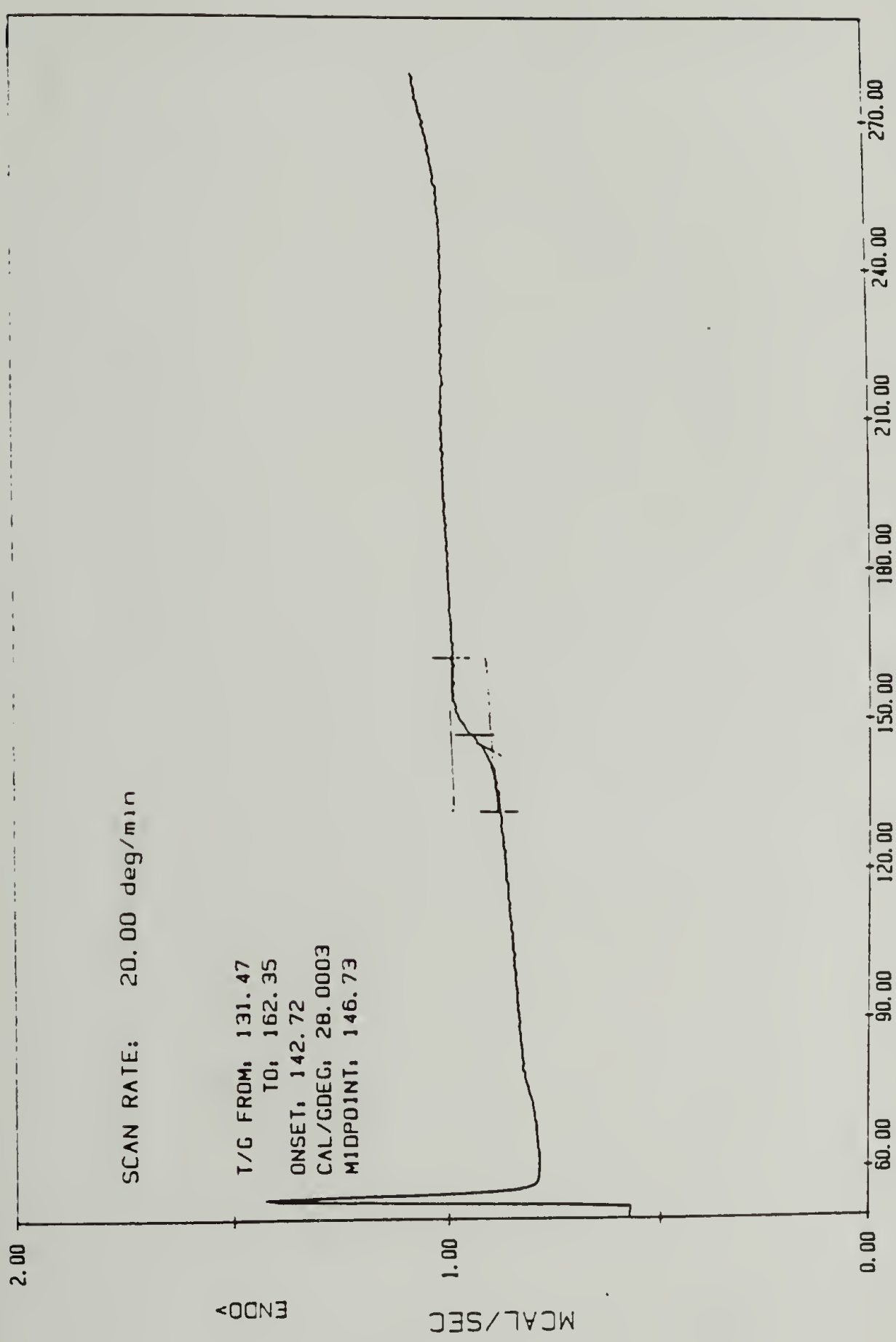


Figure 5.2 Differential Scanning Calorimeter scan of tertiarybutylhydroquinone polyetheretherketone.

superior properties to the BPAPK at comparable molecular weights. No work involving the amine functionalisation or use of this polymer in an epoxy resin formulation has been reported.

5.2 Experimental

Potassium carbonate, potassium hydroxide, tertiarybutylhydroquinone, 4,4´-difluorobenzophenone, 4-aminophenol, and diaminodiphenylsulphone (DDS) were obtained from Aldrich Chemical Company in the highest purity available. Epon 828 was obtained from Shell Chemical Company. N-methylpyrrolidinone was vacuum distilled from P_2O_5 and stored under nitrogen. Toluene was distilled from CaH_2 and stored under nitrogen.

5.2.1 Synthesis of Oligomeric Aromatic Amine Terminated Polyaryletherketone

Both the polymerization and endcapping reactions are nucleophillic aromatic substitutions (31-33). The potassium carbonate, tertiarybutylhydroquinone, and the 4,4´-difluorobenzophenone were added to a 4 neck flask equipped with a mechanical stirrer, thermometer, dean stark trap, nitrogen inlet and outlet, condenser and heating mantle. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of the solvents. N-

methylpyrrolidinone (NMP) and toluene were added via cannula. The reaction mixture was slowly heated to a stable reflux temperature of 160° C. The stoichiometry was such that a 0-5% excess of 4,4'-difluorobenzophenone was present to control molecular weight. A temperature of 160° C was maintained until all of the water of reaction had been collected (3-4 hours). Enough 4,4'-difluorobenzophenone in NMP was then added to ensure endcapping with fluorine. The reaction was continued for 1 hour after which toluene was removed quantitatively from the reaction flask. The reaction mixture was then cooled to room temperature and the polymer precipitated into methanol, washed with methanol and distilled water, then dried under vacuum. The purified oligomer was then analyzed for fluorine (appendix 6) to obtain an estimate of the number average molecular weight. In the second step the oligomeric tBUHDQPK and a stoichiometric amount of 4-aminophenol were placed into a 4 neck flask equipped as above. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of the solvents. Toluene and NMP were added via cannula. The ratio of these two solvents is such that a stable reflux temperature of 135° C is obtained (NMP/toluene = 1/1). It is important to keep the temperature as low as possible to prevent significant attack by the amine group(34). When the reaction mixture reaches 100° C a stoichiometric amount of oxygen free 50% potassium hydroxide in water is added via cannula. An excess of base must be

avoided to prevent attack by the amine at the fluorine end groups and/or attack at the carbonyls (35). A temperature of 135°C is maintained until all of the water of reaction has been collected (1.5-2 hrs). Most of the toluene is then removed from the reaction mixture through the dean stark trap. The amount of toluene remaining controls the reflux temperature. At a reflux temperature above 170°C enough toluene has been removed to allow the polymer to precipitate in the purification solvent. If enough toluene is not removed the polymer forms a toluene swollen mess which cannot be easily purified. During removal of the toluene, the time above 135°C should be kept to a minimum to prevent hemiaminal formation. The reaction mixture is then quenched to room temperature. The amine terminated oligomer is then precipitated into methanol, washed with methanol then resuspended in hot distilled water, washed with distilled water and dried under vacuum at 90°C. Elemental analysis for fluorine is again carried out to estimate the amine termination efficiency.

5.2.2 Resin Formulation

The functionalized oligomers were slowly added to the epoxy resin at 140°C while mixing vigorously. A prereaction period of 1/2 hour was allowed followed by the addition of DDS. Mixing was continued for 5 minutes. At this point, upon cooling, the resin is in a B-stage. All formulations

reported had sufficient tack and drape in this B-stage at room temperature for conventional prepreg lay up procedures. These formulations were made at amine to epoxide ratios of 1.00. The DDS containing reaction mixtures were then degassed under vacuum at 180°C for 3 to 5 minutes and transferred to preheated aluminum sheet molds also at 180°C. These resins were cured for 2 hours at 180°C followed by 2 hours at 200°C under vacuum. The sheets were then allowed to cool slowly to room temperature to minimize thermal stresses. Compact tension and three point bend samples were cut from these sheets using a jewelers slotting blade on a Bridgeport milling machine (appendix A). Precracks were inserted by an above Tg insertion technique(36).

5.2.3 Mechanical Property Characterization

Critical stress intensity factors (K_{Ic}) and fracture energy (G_{Ic}) determinations were made on compact tension samples following a modified ASTM E399-83 procedure(37-39)(appendix B). The fracture data reported may not be true K_{Ic} and G_{Ic} values as a result of the thin compact tension samples used and the uncertainty of the satisfaction of the plain strain condition assumed in the derivation of the ASTM E399 equations. Due to the very small amounts of material available for testing, an investigation into the effect of thickness could not be carried out. The fracture surfaces did not suggest plane stress conditions nor was their

significant plastic deformation prior to the initiation of crack growth since P_{max}/P_Q is ≤ 1.0. Pmax and P_Q are as defined in ASTM E399.

Young's modulus calculations were performed in three point bend following ASTM D790M (appendix C). Both determinations were carried out on an Instron testing machine at a crosshead speed of .05cm/minute. Dynamic mechanical measurements were made on an IMASS Dynastat in three point bend (appendix D). Differential scanning calorimeter (DSC) measurements were made using a Perkin Elmer DSC II.

5.3 Results and Discussion

Aromatic amine terminated tBUHDQPKs of 3,200 and 4,600 number average molecular weights and greater than 93% amine termination were incorporated into Epon 828 at various weight compositions. Table 5.1 summarizes the mechanical properties of these cured matrices. For standard deviation data see appendix G. Visible evidence for phase separation was not evident in any of the cured materials. At the higher molecular weight and the 40% loading level the cured resin was slightly cloudy but not nearly as opaque as the other polyetheretherketones investigated. The transmission electron microsopy (TEM) data shows conclusively that these tBUHDQPK resin formulations are phase separated. The domain sizes are of sufficient size to scatter visible light,

TABLE 5.1.

MECHANICAL DATA

RESINS FORMULATED USING A TERTIARYBUTYLHYDROQUINONE PEEK OF Mn = 3,200 AND AN AMINE TERMINATION EFFICIENCY OF > 91%

EPOXY RESIN	PERCENT MODIFIER	YOUNG'S MODULUS	K_{Ic} $N/M^{3/2}$	G_{Ic} J/M^2	Tg °C	PHASE SEP.	TYPE SEP.
E828	0	2.52	$.89x10^6$	315	200	No	
E828	30%	2.70	$1.6x10^6$	907	180	Micro	B
E828	40%	2.74	$1.6x10^6$	877	160	Micro	B
H69	30%	2.87	$1.5x10^6$	737	155	Micro	A
H69	40%	3.17	$1.9x10^6$	1,104	150	Micro	B

RESINS FORMULATED USING A TERTIARYBUTYLHYDROQUINONE PEEK Mn = 4,600

E828	30%	2.60	$1.5X10^6$	883	165	Micro	A/B
E828	40%	2.73	$1.9X10^6$	1,277	165	Micro	B

Phase separation type refers to phase morphology. Type A has an epoxy resin/ DDS rich continuous phase with tBUHDQPK rich inclusions. Type B has a tBUHDQPK rich continuous phase with epoxy/ DDS rich inclusions.

however very little scattering is observed. The refractive indices of the two phases therefore must be very close, resulting in very little scattering of light. Figures 5.3 to 5.5 show TEM micrographs taken of the tBUHDQPK resin formulations. The samples were prepared by room temperature microtoming followed by osmium tetroxide staining for three hours. The TEM samples were taken from bulk material away from the fracture surface. These samples were approximately 800 angstroms thick. The tBUHDQPK rich phase has a much higher density of double bonds than the epoxy/ curing agent rich phase and therefore will appear darker after staining with osmium tetroxide. In Figure 5.3 micrographs of the Epon 828/ DDS/ 3,200 Mn tBUHDQPK systems are shown. At the 30% loading the tBUHDQPK rich phase is the continuous phase having 1 by 4 micron ellipsoidal epoxy rich domains. At the 40% loading the tBUHDQPK rich phase is the continuous phase having .8 to .9 micron spherical epoxy rich domains. In Figure 5.4 micrographs of the Epon 828/ DDS/ 4,600 Mn tBUHDQPK are shown. At the 30% loading level the morphology is not clear. The tBUHDQPK rich phase forms a discontinuous / semicontinuous phase having a bimodal distribution of domain sizes. Domains of 1 micron and 16 microns are present. It appears as if the system was caught in a state of transition from an epoxy rich continuous phase to a tBUHDQPK rich continuous phase. At the 40% loading level the tBUHDQPK rich phase is the continuous phase having spherical epoxy rich 2.4 to 5 micron diameter inclusions.

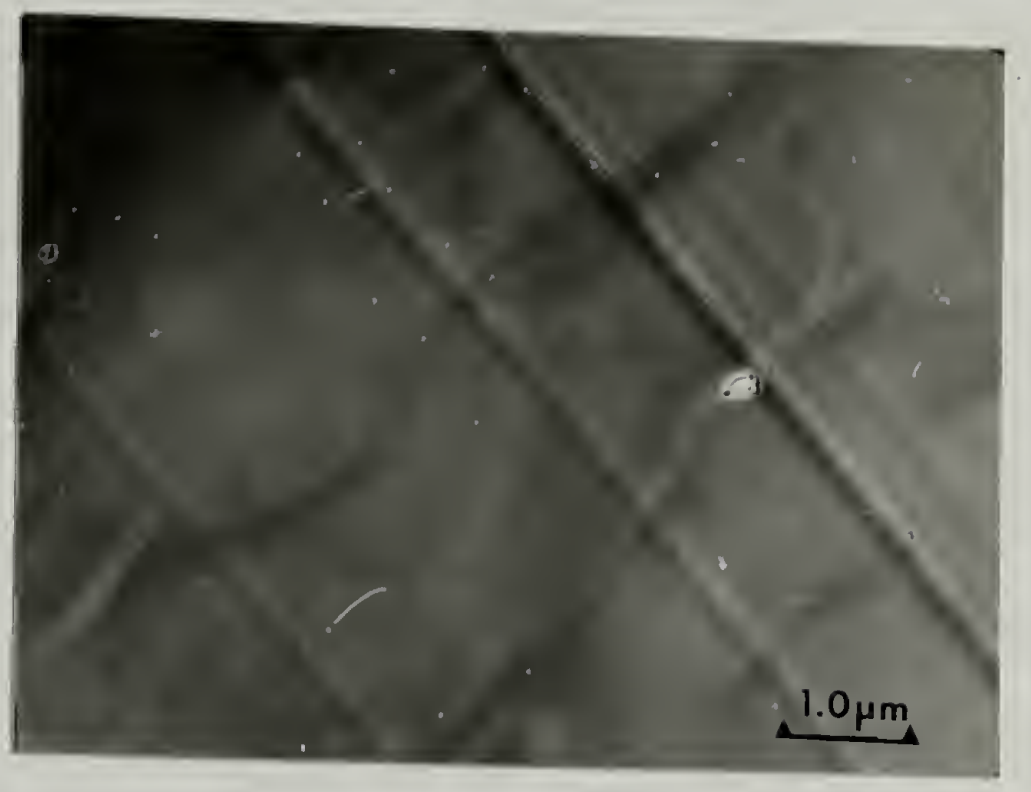
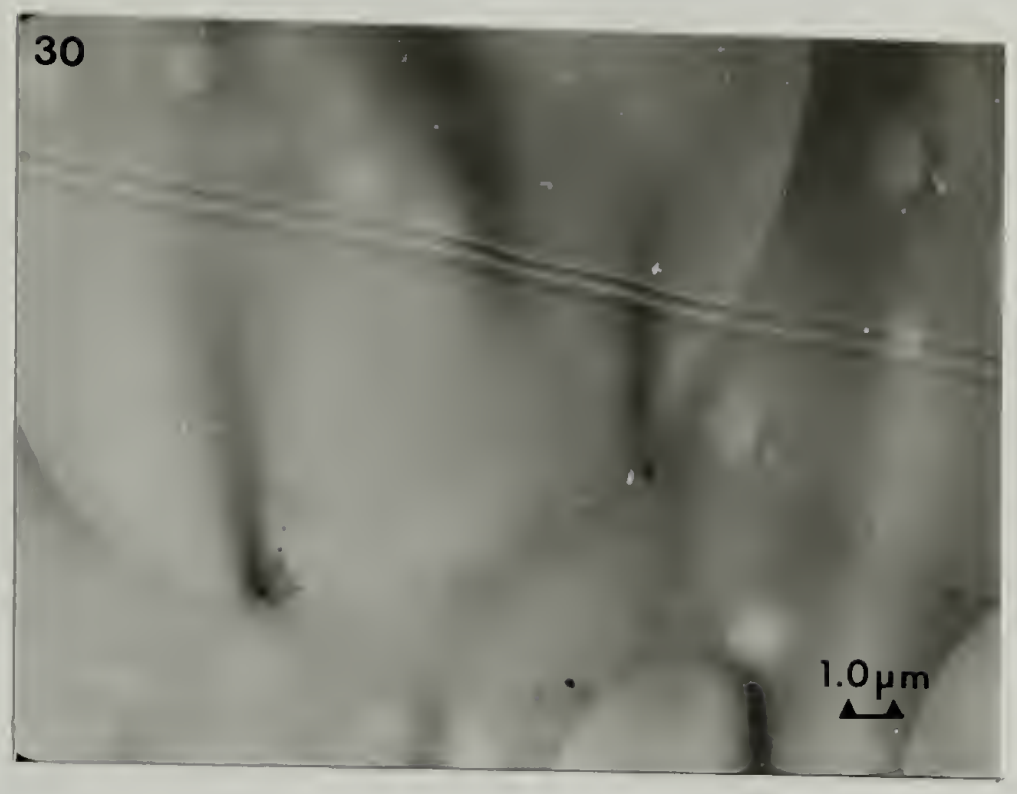


Figure 5.3 Transmission Electron Micrographs of Epon 828/ DDS/ 30% and 40% 3,200 Mn tBUHDQPK/ A/E = 1.0.



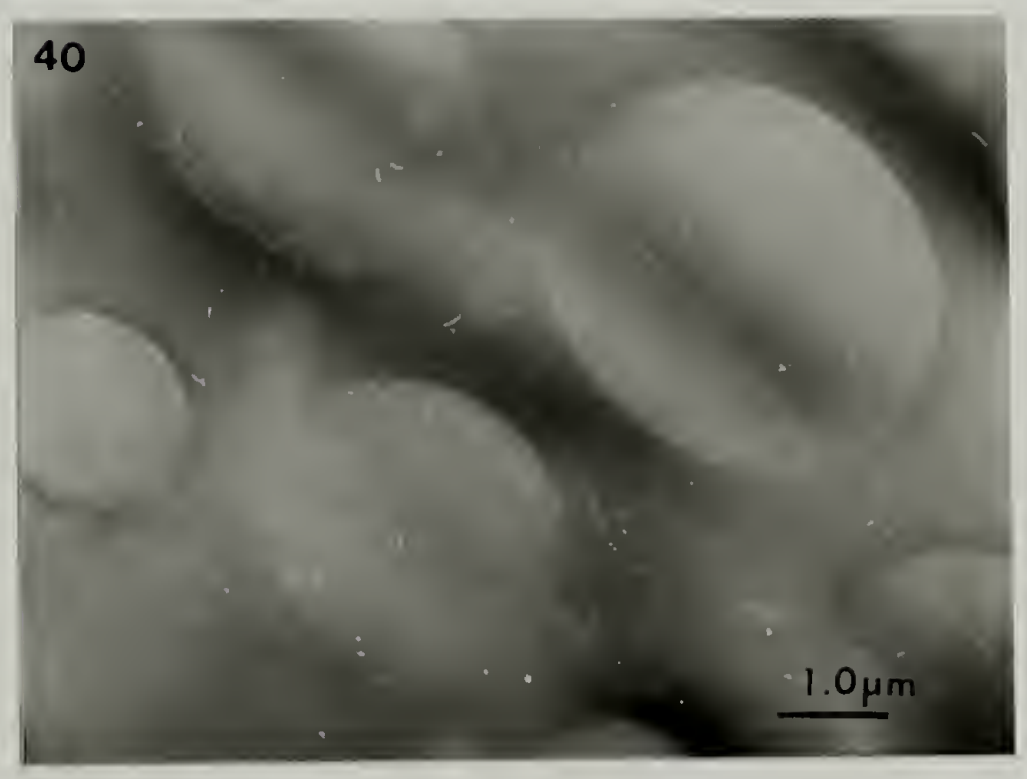


Figure 5.4 Transmission Electron Micrographs of Epon 828/ DDS/ 30% and 40% 4,600 Mn tBUHDQPK/ A/E = 1.0.

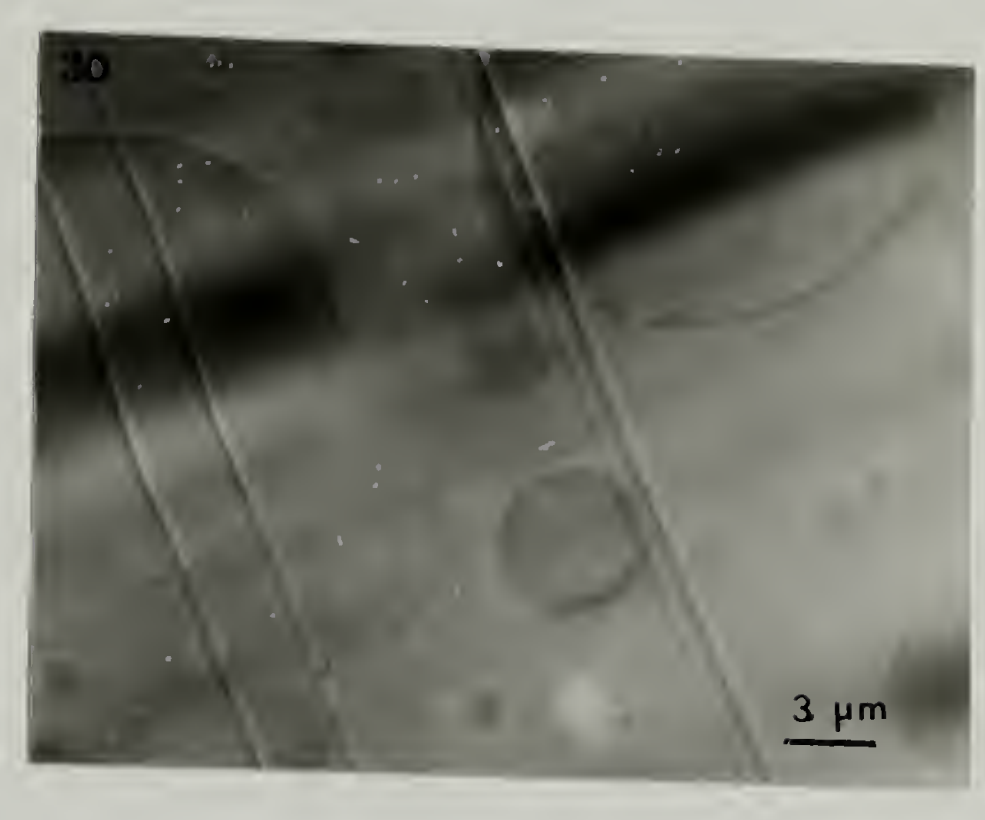


Figure 5.5 Transmission Electron Micrographs of Heloxy 69/ DDS/ 30% and 40% 3,200 Mn tBUHDQPK/ A/E = 1.0.

In Figure 5.5 micrographs of the Heloxy 69/ DDS/ 3,200 Mn tBUHDQPK system are shown. In this epoxy resin at the 30% loading level the continuous phase is epoxy rich having a bimodal distribution of spherical tBUHDQPK rich inclusions. The inclusions are .4 and 5 microns in diameter. In this epoxy resin the phase inversion level is above 30% by weight tBUHDQPK. At the 40% loading level the tBUHDQPK is now the continuous phase having a bimodal distribution of spherical epoxy rich inclusions of .6 and 5 microns in diameter.

All of the resin formulations reported had sufficient tack and drape at room temperature for conventional prepreg lay up procedures. The amount of tack and drape decreased with increasing functionalized oligomer weight fraction. In all of the resin formulations it was discovered that K_{Ic} and G_{Ic} increased with the weight percent and molecular weight of the amine terminated tBUHDQPK added. Figure 5.6. is a plot of K_{Ic} vs. weight concentration of the functionalized oligomer for the 3,200 and 4,600 number average molecular weight tBUHDQPKs. Increases in the K_{Ic} values of 80% were obtained for the 3,200 Mn tBUHDQPK at the 30% and 40% weight loadings in Epon 828. In Heloxy 69 a 68% and 113% increase were obtained at the 30 and 40% loading levels of the 3,200 Mn tBUHDQPK. Increases in the K_{Ic} values of 68% and 113% were also obtained for the 4,600 Mn tBUHDQPK at weight loadings of 30% and 40% respectively in Epon 828. The improvements in K_{Ic} are approximately double when the tBUHDQPK forms the continuous phase. In Figure 5.7 a plot

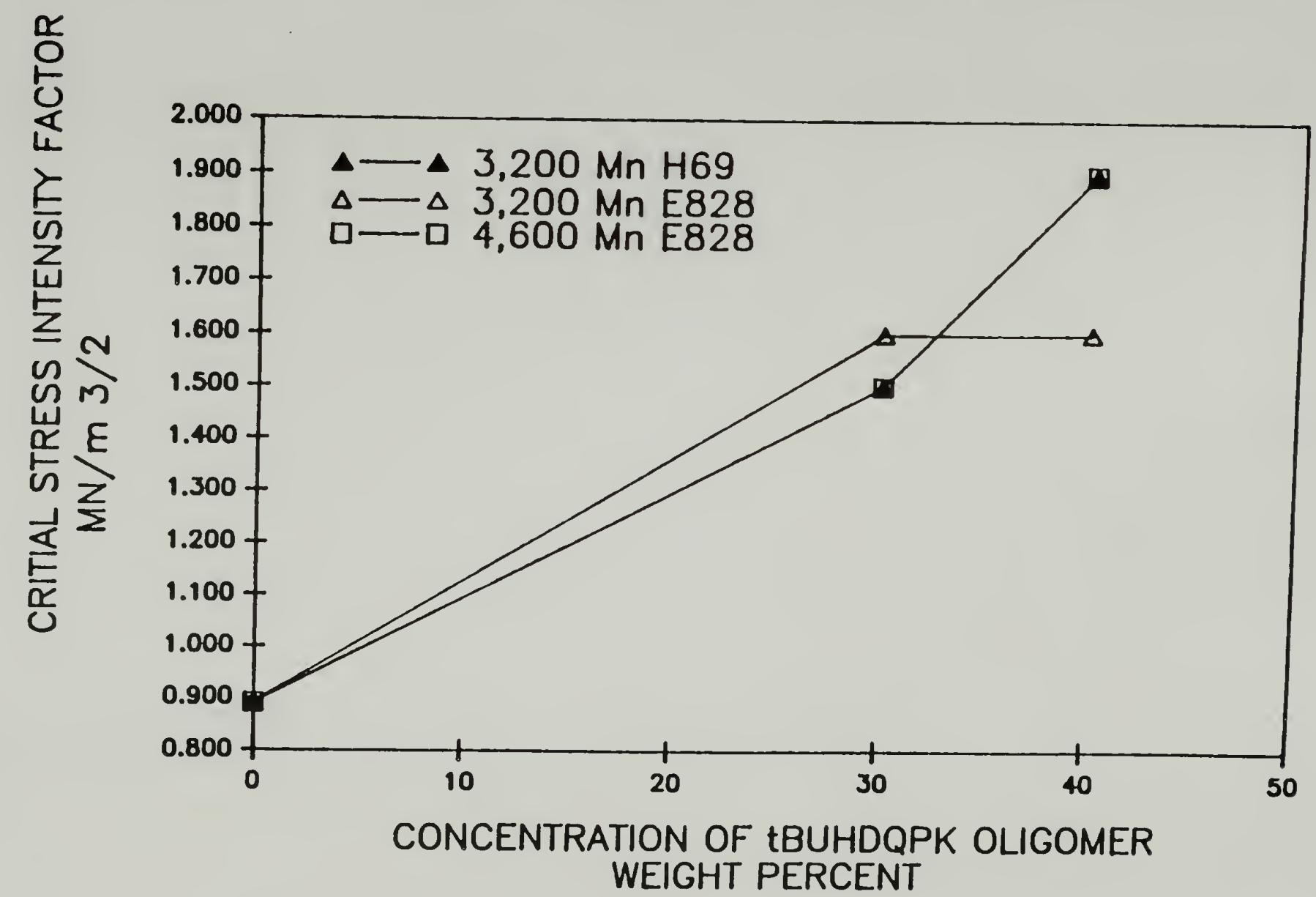


Figure 5.6 Critical Stress Intensity Factor vs. Concentration for the 3,200 Mn and 4,600 Mn tBUHDQPKs in Epon 828 and Heloxy 69 cured with DDS at an A/E of 1.0.

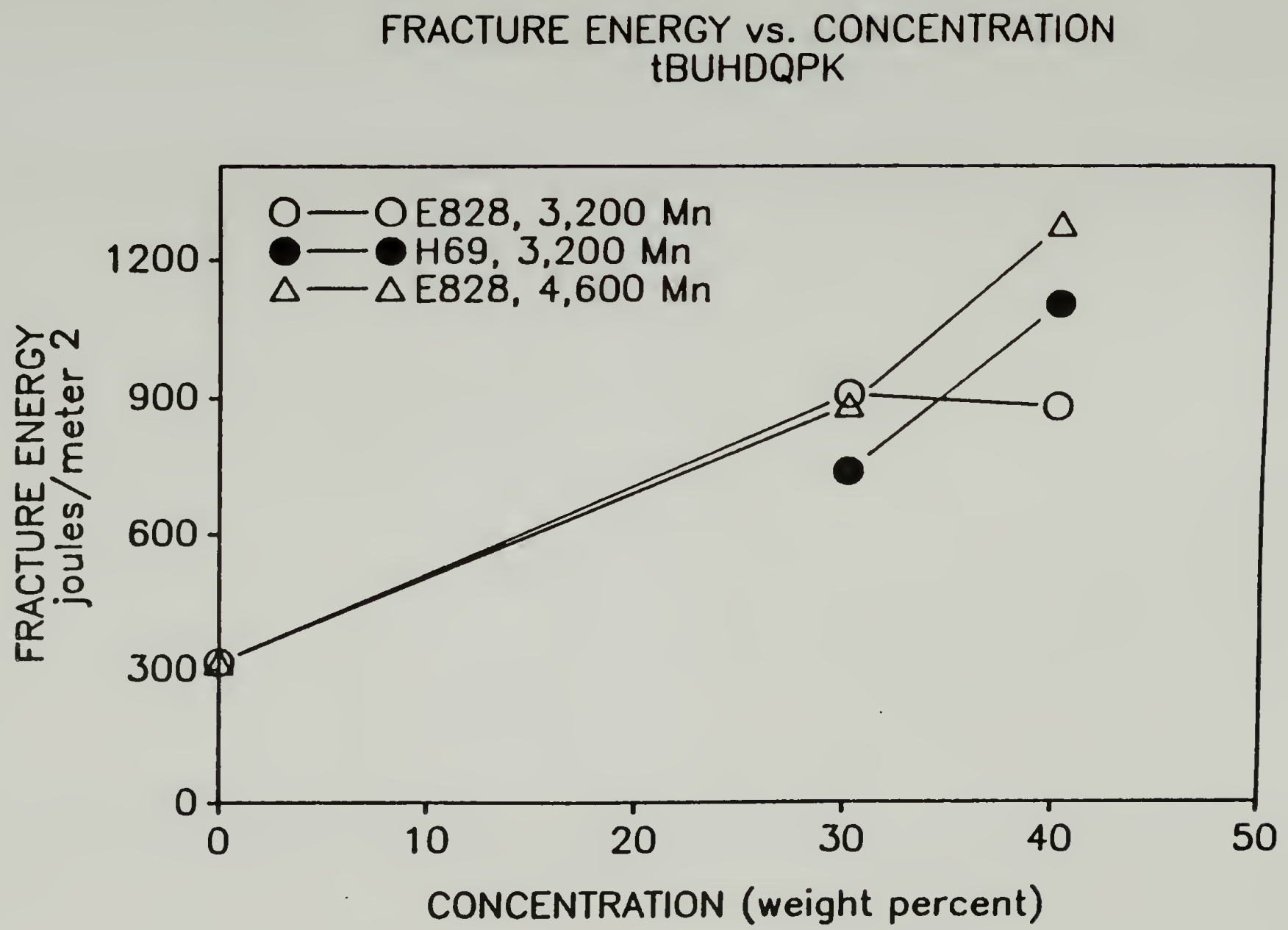


Figure 5.7 Fracture Energy vs. Concentration for the 3,200 Mn and 4,600 Mn tBUHDQPKs in Epon 828 and Heloxy 69 cured with DDS at an A/E of 1.0.

of G_{Ic} vs. the weight concentration of tBUHDQPK is shown for the 3,200 Mn and 4,600 Mn tBUHDQPK samples. Figure 5.8 is a plot of Young's modulus versus weight percent functionalized oligomer for both the 3,200 and 4,600 Mn oligomers. An increase in Young's modulus of 9 percent was obtained for the 30 and 40% weight loading levels of the 3,200 Mn tBUHDQPK in Epon 828. In Heloxy 69 the 3,200 Mn tBUHDQPK at the 30 and 40% weight loadings increased Young's modulus by 14% and 26% respectively. At the higher molecular weight the tBUHDQPK did not significantly change the modulus of the materials.

In Figures 5.9 and 5.10 load deflection curves for three point bend beams are shown for the 4,600 Mn tBUHDQPK in Epon 828 at 30 and 40 percent by weight respectively. Both samples exhibit failure after some plastic deformation. Fracture surfaces are whitened by this plastic flow.

Figures 5.11-5.17 are plots of the dynamic storage and loss moduli and loss tangent vs. temperature for the cured resin formulations. Figure 5.11. represents the Epon 828/ DDS neat resin. In this figure a glass transition temperature of 220°C is observed. In Figures 5.12 and 5.13 the dynamic mechanical properties for the Epon 828/ DDS/ 30% and 40% 3,200 Mn tBUHDQPK are shown. This data shows glass transition temperatures of 170°C and 165°C respectively. Figures 5.14 and 5.15 represent the Epon 828/ DDS/ 30% and 40% 4,600 Mn tBUHDQPK formulations. Glass transition temperatures of 170°C and 165°C were measured respectively.

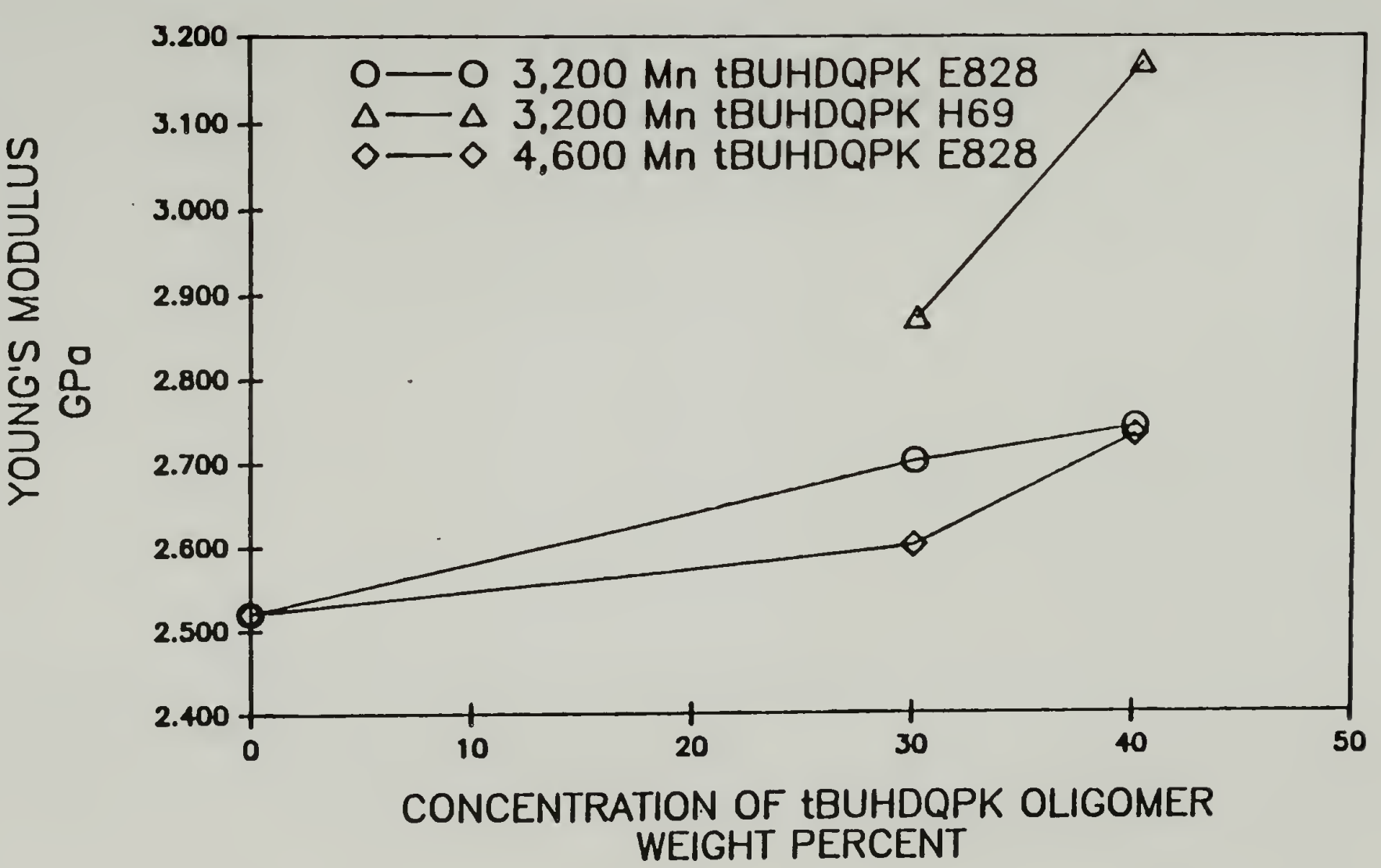


Figure 5.8 Young's Modulus vs. Concentration of the 3,200 Mn and 4,600 Mn tBUHDQPKs in Epon 828 and Heloxy 69 cured with DDS at an A/E of 1.0.

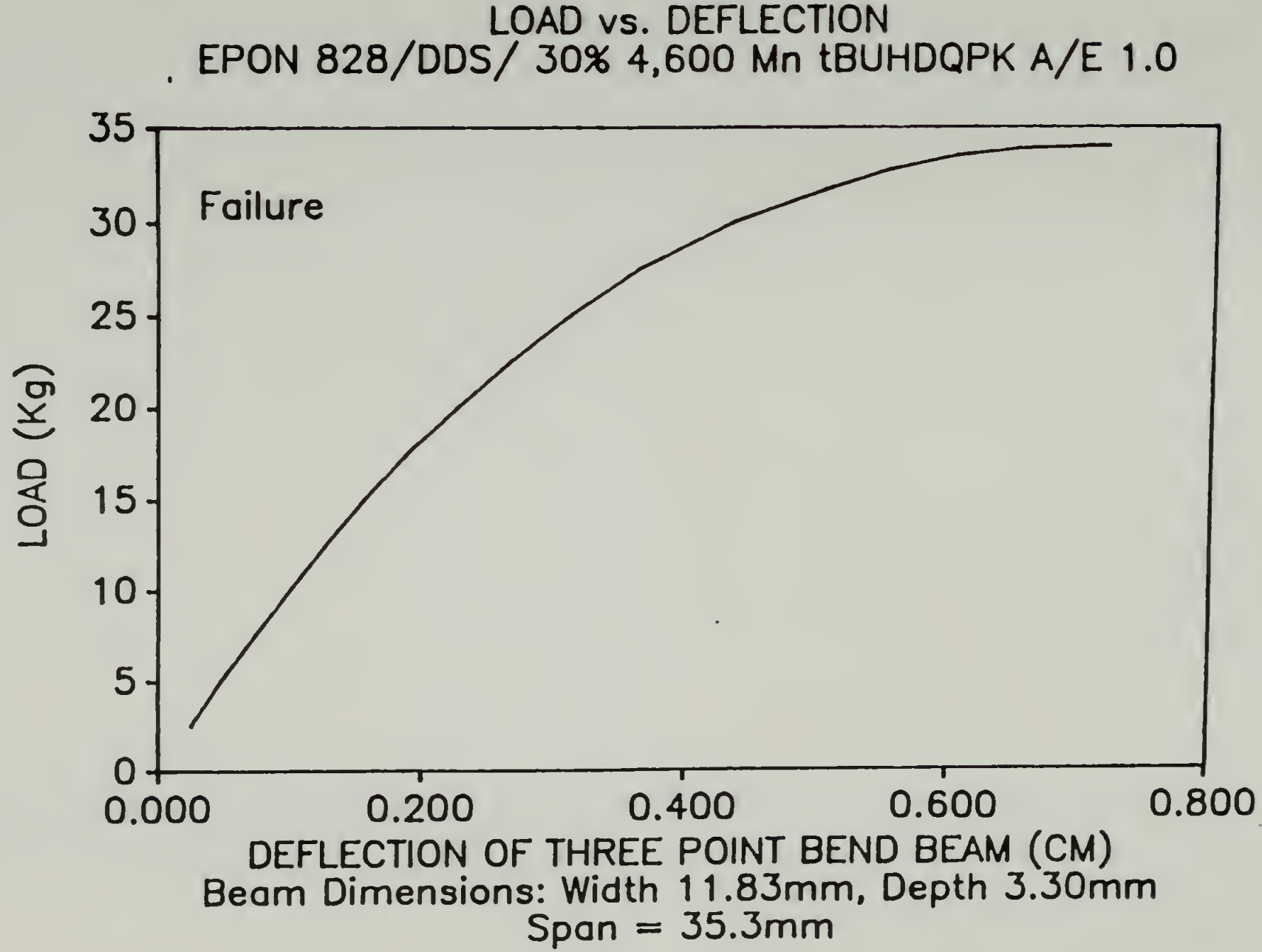


Figure 5.9 Load vs. Deflection of a three point bend beam of Epon 828/ DDS/ 30% 4,600 Mn tBUHDQPK/ A/E = 1.0.

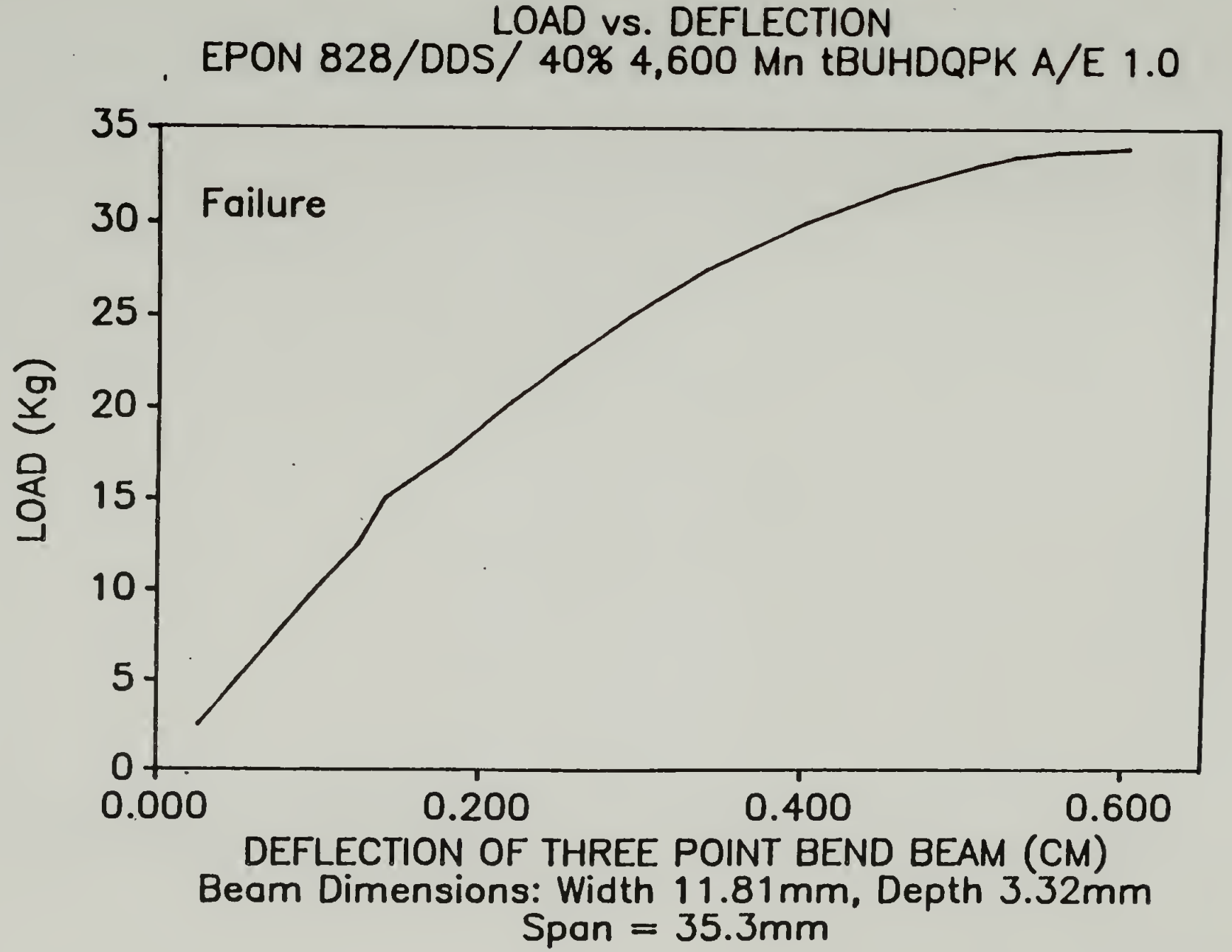


Figure 5.10 Load vs. Deflection of a three point bend beam of Epon 828/ DDS/ 40% 4,600 Mn tBUHDQPK/ A/E = 1.0.

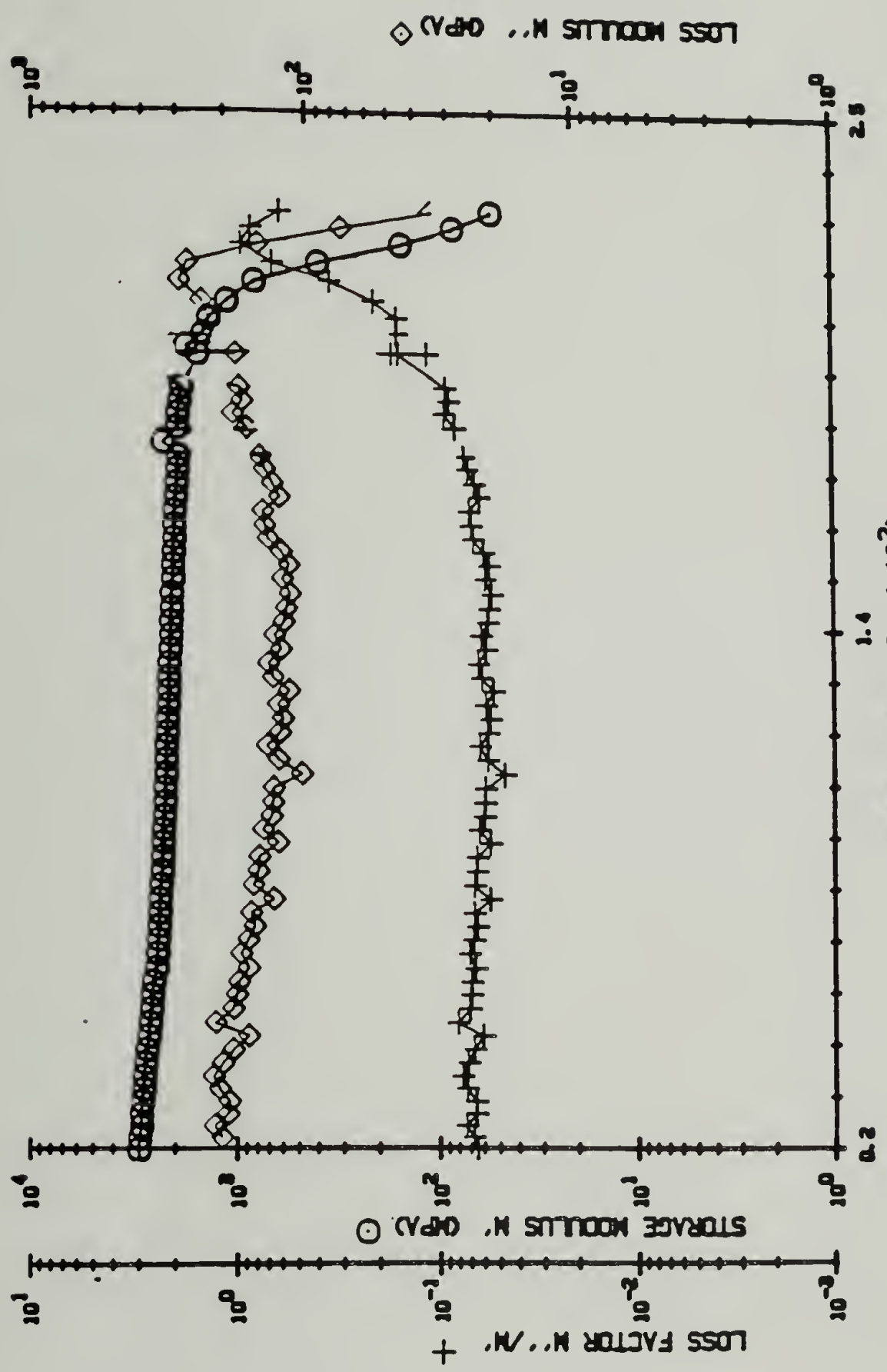


Figure 5.11 Dynamic Mechanical Properties of Epon 828/DDS/ A/E = 1.0.

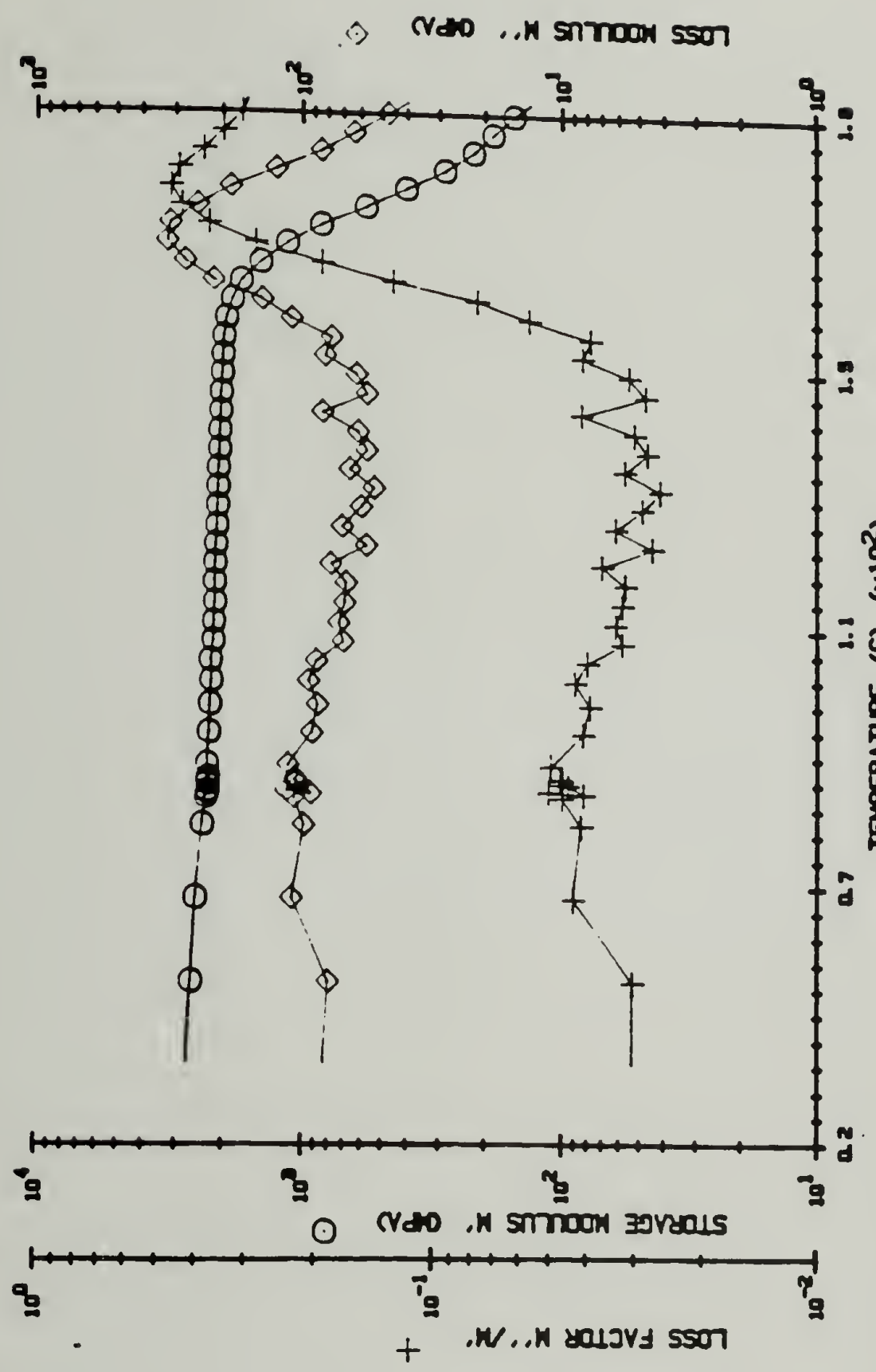


Figure 5.12 Dynamic Mechanical Properties of Epon 828/DDS/ 30% 3,200 Mn tBUHDQPK/ A/E = 1.0.

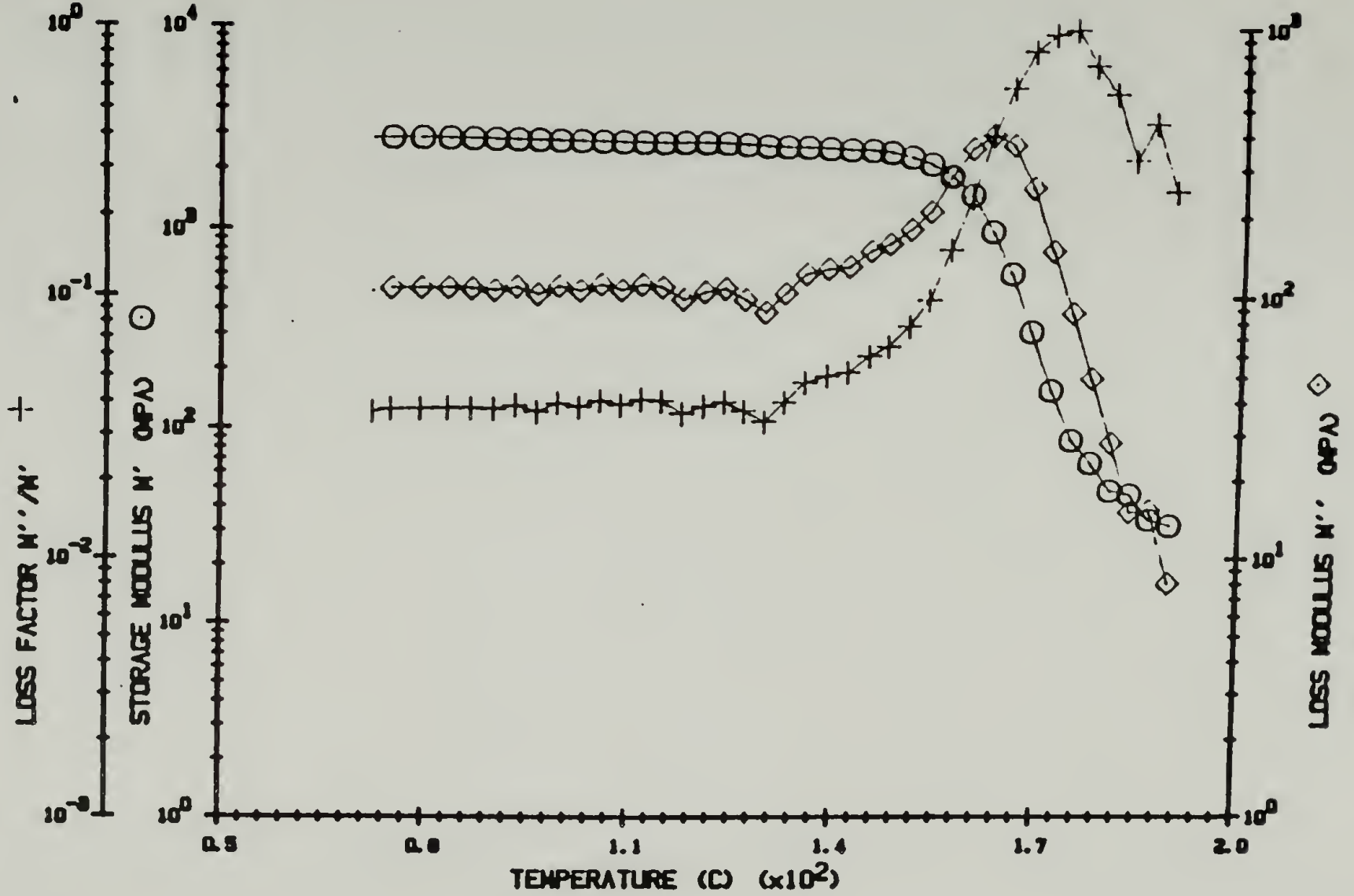


Figure 5.13 Dynamic Mechanical Properties of Epon 828/DDS/ 40% 3,200 Mn tBUHDQPK/ A/E = 1.0.

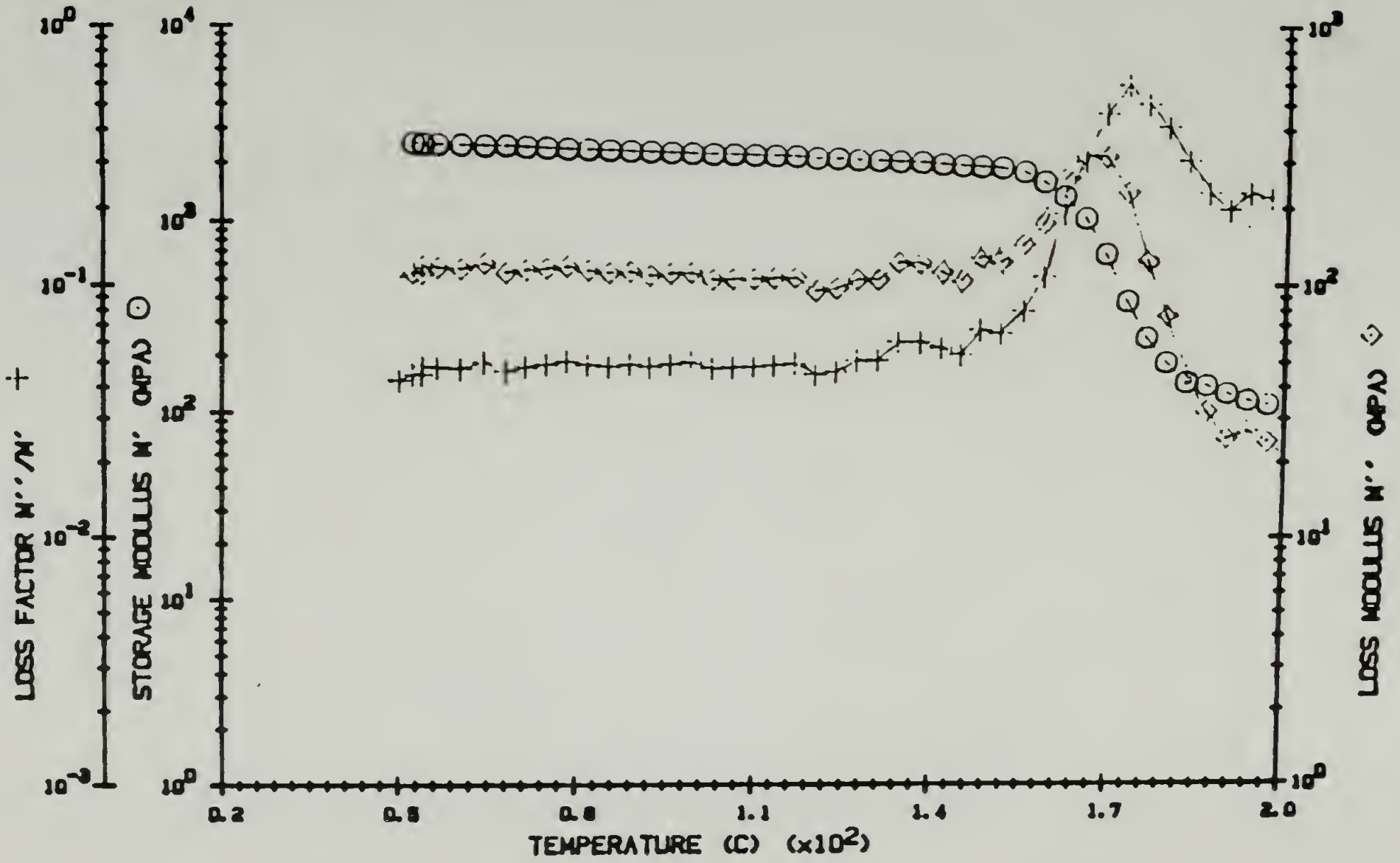


Figure 5.14 Dynamic Mechanical Properties of Epon 828/DDS/ 30% 4,600 Mn tBUHDQPK/ A/E = 1.0.

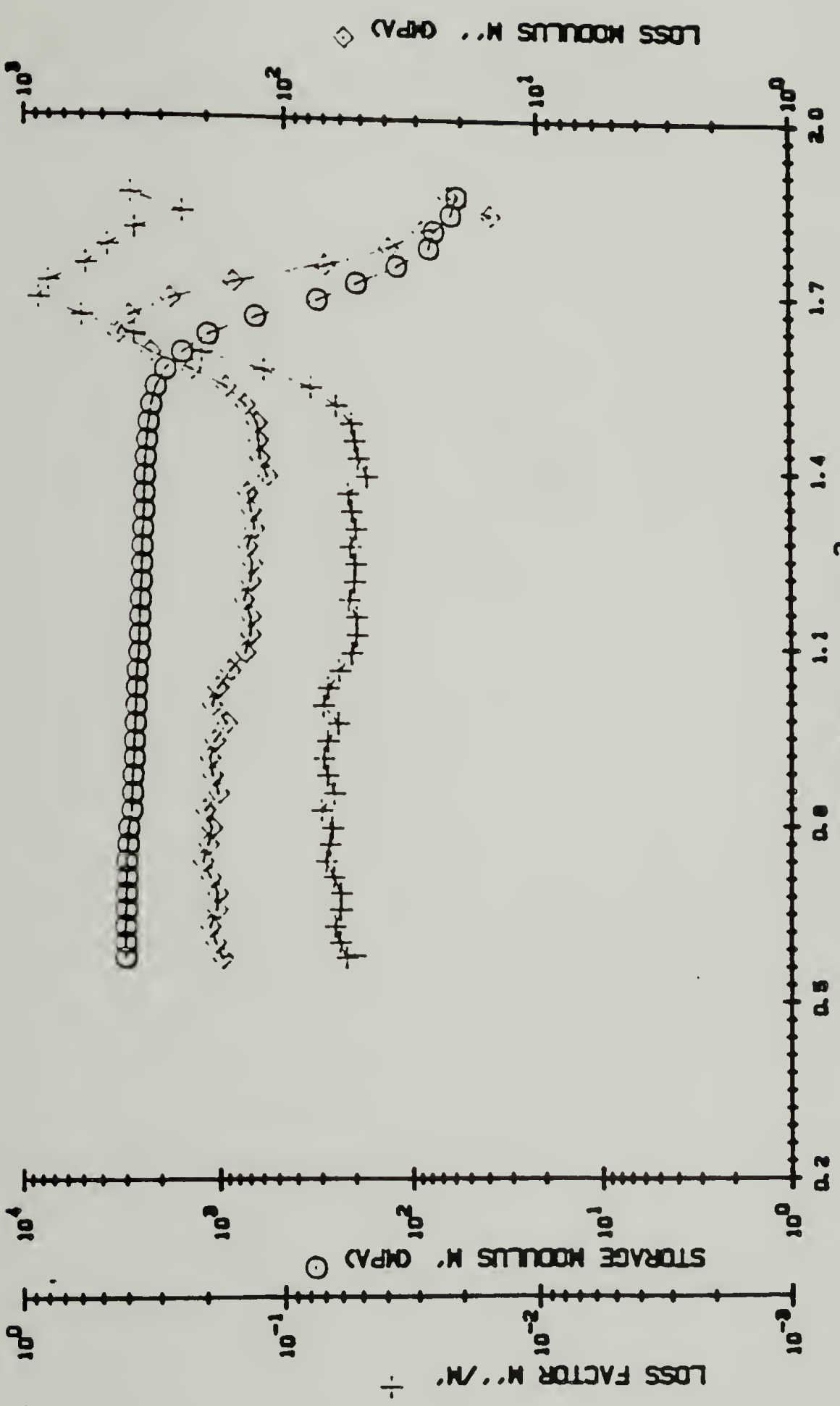


Figure 5.15 Dynamic Mechanical Properties of Epon 828/DDS/ 40% 4,600 Mn tBUHDQPK/ A/E = 1.0.

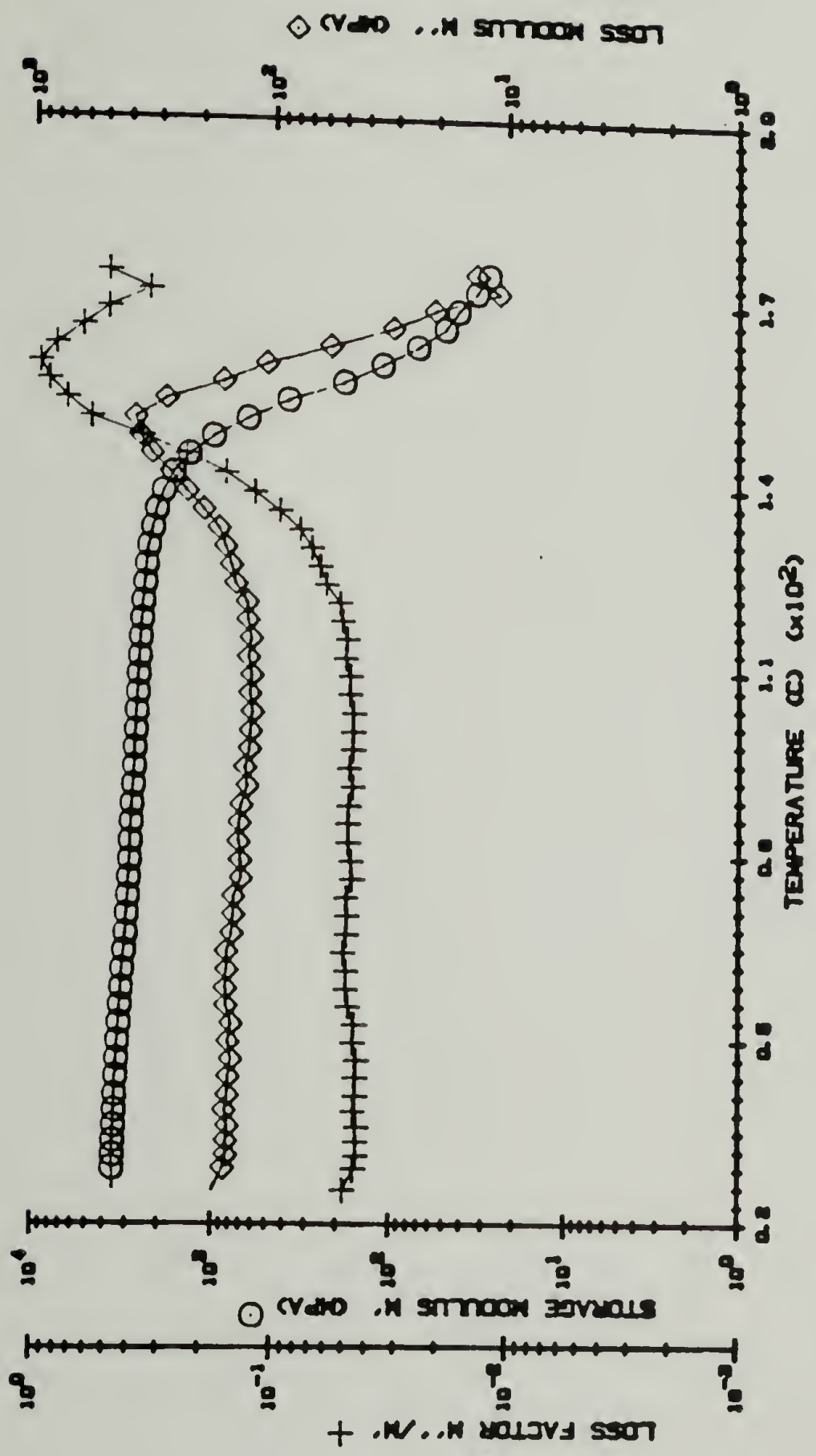


Figure 5.16 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 30% 3,200 Mn tBUHDQPK/ A/E = 1.0.

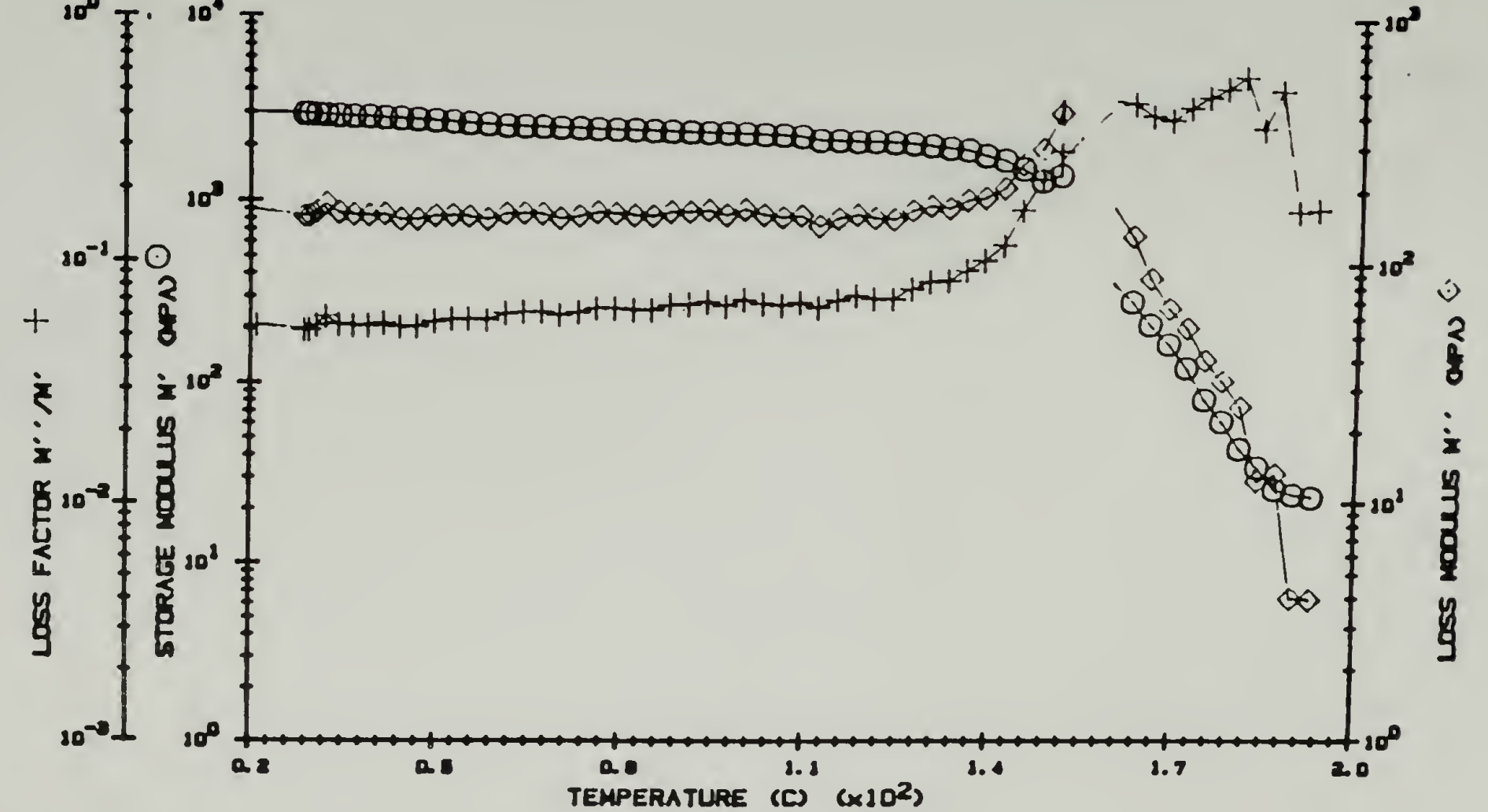


Figure 5.17 Dynamic Mechanical Properties of Heloxy 69/ DDS/ 40% 3,200 Mn tBUHDQPK/ A/E = 1.0.

Figures 5.16 and 5.17 represent the Heloxy 69/ DDS/ 30% and 40% 3,200 Mn tBUHDQPK formulations. Glass transition temperatures of 155°C and 150°C were obtained respectively. Again a decrease in the glass transition temperature with increased weight percent functionalized oligomer is observed.

Despite the phase separation only one glass transition is seen in each of the cured modified resins. This is the result of the inherent insensitivity of the Dynastat when used in three point bend samples of this thickness. At the first glass transition the drop in stiffness is so severe that the machine can no longer detect slight material changes. This glass transition temperature information is listed in Table 5.1.

5.4 Conclusions

A tough matrix material can be achieved via the incorporation of an oligomeric end functionalized tertiarybutylhydroquinone based polyetheretherketone into a commercial epoxy resin while maintaining processability. Higher molecular weight functionalized oligomers yield higher K_{Ic} values. The substantial increase in resistance to fracture, while maintaining a modulus of 2-3 Gpa makes these materials very attractive for composite use. It is known from the TEM data that these materials behave similarly to the amine terminated polyethersulphone (ATPEES)

systems where at low percent incorporations the phase separated morphology consists of an epoxy matrix with ATPEES rich inclusions and at high percent incorporations the matrix is ATPEES rich and the inclusions are epoxy rich (23-26). As expected the greatest resistance to fracture is attained when the continuous phase is rich in the oligomeric thermoplastic. For Heloxy 69 the phase inversion point is above 30% by weight 3,200 Mn tBUHDQPK. For Epon 828 the phase inversion point is below 30% by weight at both 3,200 and 4,600 Mn tBUHDQPK. In the tBUHDQPK/ epoxy systems at the lower loading level (<30% in Epon 828 and <40% in Heloxy 69) the cured resin consists of tBUHDQPK rich inclusions in an epoxy/curing agent rich matrix. In this situation the tBUHDQPK rich inclusions act as stress concentrators in the matrix. These stress concentrations should be small as a result of the similarity in the tensile, shear, and bulk moduli of the two phases. These small stress concentrations may cause the initiation of localized shear yielding in the matrix resulting in increases in the resistance to crack propagation. These inclusions also have the ability to deform in a ductile manner thereby increasing the energy required for crack propagation further. Energy absorption is further facilitated by the presence of some tBUHDQPK in the epoxy rich continuous phase, acting to increase the molecular weight between crosslinks and therefore molecular mobility. At the higher loading levels there is a phase inversion in which the inclusions are now epoxy/curing agent

rich and the matrix is tBUHDQPK rich. In this morphology the distance between crosslinks in the matrix is greatly increased, allowing for the chain mobility required for large energy absorbing deformations. Therefore at these high loading levels the inherent level of ductility of the material is greatly increased and is responsible for the observed tremendous increases in resistance to fracture. Deformations become similar to those found in the parent aromatic thermoplastic material, failure is ductile. The phase inverted morphology should also lead to greater resistance to water and deicing fluid as in the BPAPK formulations. Similarly these resin formulations would be expected to absorb large amounts of methylene chloride and methyl ethyl ketone. The behavior of the highest loading levels would be expected to mimic that of the tBUHDQPK homopolymer. In this phase inverted morphology the matrix material can be more correctly considered a "processable, thermosetting tertiarybutylhydroquinone PEEK " rather than a toughened epoxy. The glass transition temperature (Tg) of the modified Epon 828 resins at the higher loading levels is 160° C. This Tg is sufficiently high for high performance composite use. The K_{Ic} and G_{Ic} values obtained are higher than those obtained with the BPAPK at comparable number average molecular weights.

In conclusion,the formulations in Table 5.1 are equal in fracture resistance to the toughest, processable high glass transition thermosetting matrix resins developed in

other laboratories to date. High fracture resistance results from the ductility of the tBUHDQPK rich continuous phase.

CHAPTER 6

RESORCINOL BASED POLYARYLETHERKETONE AS A MATRIX MODIFIER WITH EPOXY RESINS

6.1 Introduction

The polyetheretherketone made from the reaction of resorcinol with 4,4′-difluorobenzophenone is an amorphous polymer having a glass transition temperature of 105°C. The structure of this polymer in the amine terminated form is+ shown in Figure 6.1. Figure 6.2. is a DSC scan of this material. This polymer behaves in a similar fashion to the other two amorphous polyetheretherketones investigated (BPAPK and tBUHDQPK). Resorcinol polyetheretherketone (RESPK) is soluble in an NMP / toluene mixture below 100°C and therefore is easily amine terminated with 4-aminophenol at 135°C. The resulting aromatic amine terminated species is readily soluble in Epon 828 at 120°C.

6.2 Experimental

Potassium carbonate, potassium hydroxide, resorcinol, 4,4′-difluorobenzophenone, 4-aminophenol, and diamino diphenyl sulphone (DDS) were obtained from Aldrich Chemical Company in the highest purity available. Epon 828 was obtained from Shell Chemical Company. N-methylpyrrolidinone

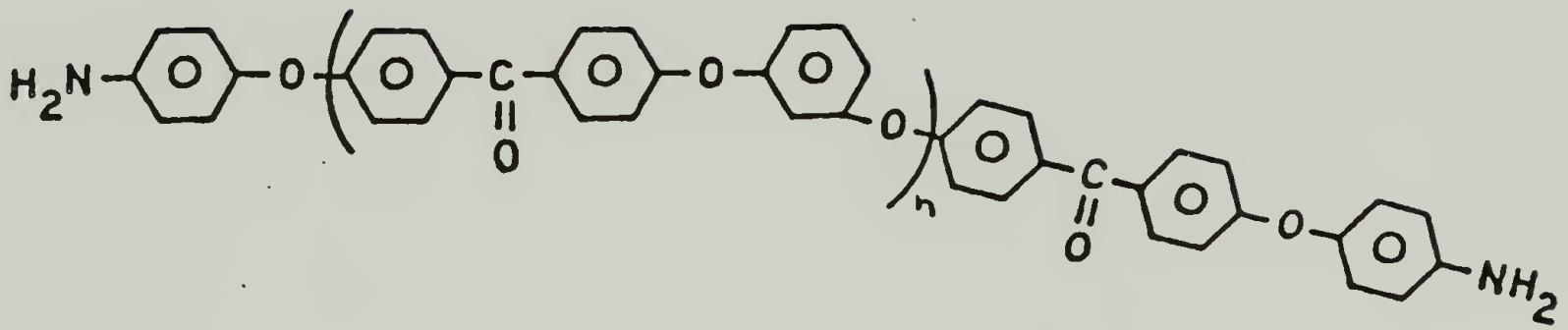


Figure 6.1
RESORCINOL POLYETHERETHERKETONE

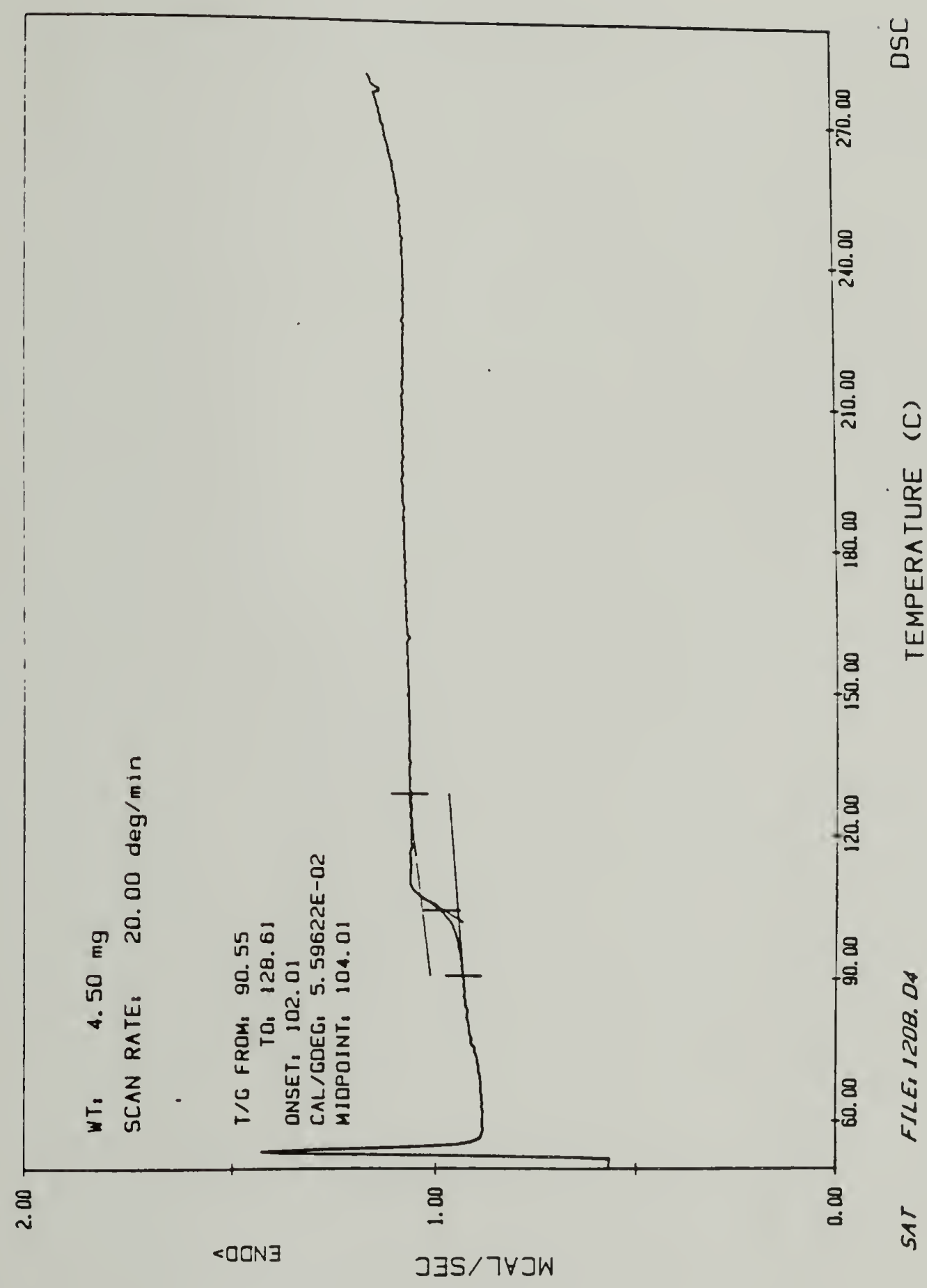


Figure 6.2 Differential Scanning Calorimeter Scan of Resorcinol polyetheretherketone.

was vacuum distilled from P_2O_5 and stored under nitrogen. Toluene was distilled from CaH_2 and stored under nitrogen.

6.2.1 Synthesis of Oligomeric Aromatic Amine Terminated Polyaryletherketone

Both the polymerization and endcapping reactions are nucleophillic aromatic substitutions (31-33). The potassium carbonate, resorcinol, and the 4,4´-difluorobenzophenone were added to a 4 neck flask equipped with a mechanical stirrer, thermometer, dean stark trap, nitrogen inlet and outlet, condenser and heating mantle. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of the solvents. N-methylpyrrolidinone (NMP) and toluene were added via cannula. The reaction mixture was slowly heated to a stable reflux temperature of 160°C. The stoichiometry was such that 0-5% excess of 4,4´-difluorobenzophenone was present to control molecular weight. A temperature of 160°C was maintained until all of the water of reaction had been collected (3-4 hours). Enough 4,4´-difluorobenzophenone in NMP was then added to ensure endcapping with fluorine. The reaction was continued for 1 hour after which toluene was removed quantitatively from the reaction flask. The reaction mixture was then cooled to room temperature and the polymer precipitated into methanol, washed with methanol and water, then dried under vacuum. The purified oligomer was then analyzed for

fluorine (appendix 6) to obtain an estimate of the number average molecular weight. In the second step the oligomeric RESPK and a stoichiometric amount of 4-aminophenol were placed into a 4 neck flask equipped as above. The flask was purged continuously with nitrogen starting 20 minutes prior to the addition of the solvents. Toluene and NMP were added via cannula. The ratio of these two solvents is such that a stable reflux temperature of 135°C is obtained (NMP/toluene = 1/1). It is important to keep the temperature as low as possible to prevent significant attack by the amine group(34). It also seems important to keep the oxygen in the flask to a minimum to prevent oxidation of the 4-aminophenol. When the reaction mixture reaches 100°C a stoichiometric amount of oxygen free 50% potassium hydroxide in water is added via cannula. An excess of base must be avoided to prevent attack by the amine at the fluorine end groups and/or attack at the carbonyls (35). A temperature of 135°C is maintained until all of the water of reaction has been collected (1.5-2 hrs). Most of the toluene is then removed from the reaction mixture through the dean stark trap. The amount of toluene removed is measured by the reflux temperature. At a reflux temperature above 170°C enough toluene has been removed to allow the polymer to precipitate in the purification solvent. If enough toluene is not removed the polymer forms a toluene swollen mess which cannot be easily purified. After removal of the toluene, during which the time above 135°C should be kept to

a minimum to prevent hemiaminal formation, the reaction mixture is quenched to room temperature. The amine terminated oligomer is then precipitated into methanol, washed with methanol, resuspended in distilled water, washed with distilled water and dried under vacuum at 90°C. Elemental analysis for fluorine is again carried out to estimate the amine termination efficiency.

6.2.2 Resin Formulation

The functionalized oligomers were slowly added to the epoxy resins at 140°C while mixing vigorously. A prereaction period of 1/2 hour was allowed followed by the addition of DDS. Mixing was continued for 5 minutes. At this point, upon cooling, the resin is in a B-stage. All formulations reported had sufficient tack and drape in this B-stage at room temperature for conventional prepreg lay up procedures. These formulations were made at an amine to epoxide ratio of 1.0. The DDS containing reaction mixtures were then degassed under vacuum at 180°C for 3 to 5 minutes and transferred to preheated aluminum sheet molds also at 180°C. These resins were cured for 2 hours at 180°C followed by 2 hours at 200°C under vacuum. The sheets were then allowed to cool slowly to room temperature to minimize thermal stresses. Compact tension and three point bend samples were cut from these sheets using a jewelers slotting

blade on a Bridgeport milling machine (appendix A). Precracks were inserted by a above Tg insertion technique (36).

6.2.3 Mechanical Property Characterization

Critical stress intensity factors (K_{Ic}) and fracture energy (G_{Ic}) determinations were made on compact tension samples following a modified ASTM E399-83 procedure(37-39)(appendix B). The fracture data reported may not be true K_{Ic} and G_{Ic} values as a result of the thin compact tension samples used and the uncertainty of the satisfaction of the plain strain condition assumed in the derivation of the ASTM E399 equations. Due to the very small amounts of material available for testing, an investigation into the effect of thickness could not be carried out. The fracture surfaces did not suggest plane stress conditions nor was their significant plastic deformation prior to the initiation of crack growth since P_{max}/P_Q is ≤ 1.0. P_{max} and P_Q are as defined in ASTM E399.

Young's modulus calculations were performed in three point bend following ASTM D790M (appendix C). Both determinations were carried out on an Instron testing machine at a crosshead speed of .05cm/minute. Dynamic mechanical measurements were made on an IMASS Dynastat in three point bend (appendix D). Differential scanning

calorimeter (DSC) measurements were made using a Perkin Elmer DSC II.

6.3 Results and Discussion

Aromatic amine terminated RESPKs of 3,400 and 7,000 number average molecular weight and greater than 92% amine termination were incorporated into Epon 828 at various weight compositions. Table 6.1 summarizes the mechanical properties of these cured matrices. For standard deviation data see appendix G. Phase separation was visibly evident in all of the cured materials. In the Epon 828 formulations the cured resins were opaque suggesting phase separation into domains on the order of the wavelength of visible light.

An attempt to further characterize the phase morphology of these RESPK containing formulations was made using transmission electron microscopy on 800 angstrom samples which had been stained with osmium tetroxide. Although the RESPK system did not appreciably differ in double bond density from the tBUHDQPK systems no preferential staining was observed. The TEM micrographs appeared featureless. Therefore no estimate of domain size or phase morphology was possible.

All of the formulations made using the 3,400 Mn RESPK had sufficient tack and drape at room temperature for conventional prepreg lay up procedures. The formulations

TABLE 6.1

RESINS FORMULATED USING A RESORCINOL PEEK OF Mn = 3,400 AND AMINE TERMINATION EFFICIENCY OF > 92%

EPOXY RESIN	PERCENT MODIFIER	YOUNG'S MODULUS	K_{IC} $N/M^{3/2}$	G_{IC} J/M^2	Tg ^oC	PHASE SEP.	TYPE SEP.
E828	0	2.52	$.89x10^6$	315	200	No	
E828	30%	2.84	$1.1x10^6$	433	180	Micro	UK
E828	40%	2.77	$1.2x10^6$	529	160	Micro	UK

RESINS FORMULATED USING A RESORCINOL PEEK OF Mn = 7,000

E828	30%	2.61	$1.0X10^6$	395	155	Micro	UK
E828	40%	TOO VISCOUS TO PROCESS					

Phase type refers to phase morphology. UK signifies that the phase morphology is unknown.

made with the 7,000 Mn RESPK had drape but no tack at room temperature, however at 60°C both tack and drape were present. The amount of tack and drape decreased with increasing functionalized oligomer weight fraction. It was discovered that K_{Ic} and G_{Ic} increased with the weight percent amine terminated 3,400 Mn RESPK added. Figure 6.3. is a plot of K_{Ic} vs. weight concentration of the functionalized 3,400 Mn and 7,000 Mn oligomers for the Epon 828 formulations. Increases in K_{Ic} of 24% and 35% were obtained for the 30% and 40% loadings respectively of the 3,400 Mn oligomer. An increase of 12% was obtained for the 7,000 Mn oligomer at 30% by weight loading. This oligomer was not processable at the 40% loading level. Once again a dependence of K_{Ic} on percent loading is observed. No dependence on number average molecular weight can be ascertained. Figure 6.4 contains a plot of G_{Ic} vs. weight concentration of the functionalized 3,400 and 7,000 Mn RESPK oligomers. In Figure 6.5 a plot of Young's modulus versus weight concentration of the 3,400 Mn RESPK is shown. Once again Young's modulus is observed to increase with the concentration of low molecular weight oligomer added. Figures 6.6.-6.8. are plots of the dynamic storage and loss moduli and loss tangent vs. temperature for the cured resin formulations. From the dynamic mechanical data it was observed that the glass transition temperature decreased with increasing weight percent functionalized 3,400 and 7,000 Mn oligomers. The glass transition temperature was

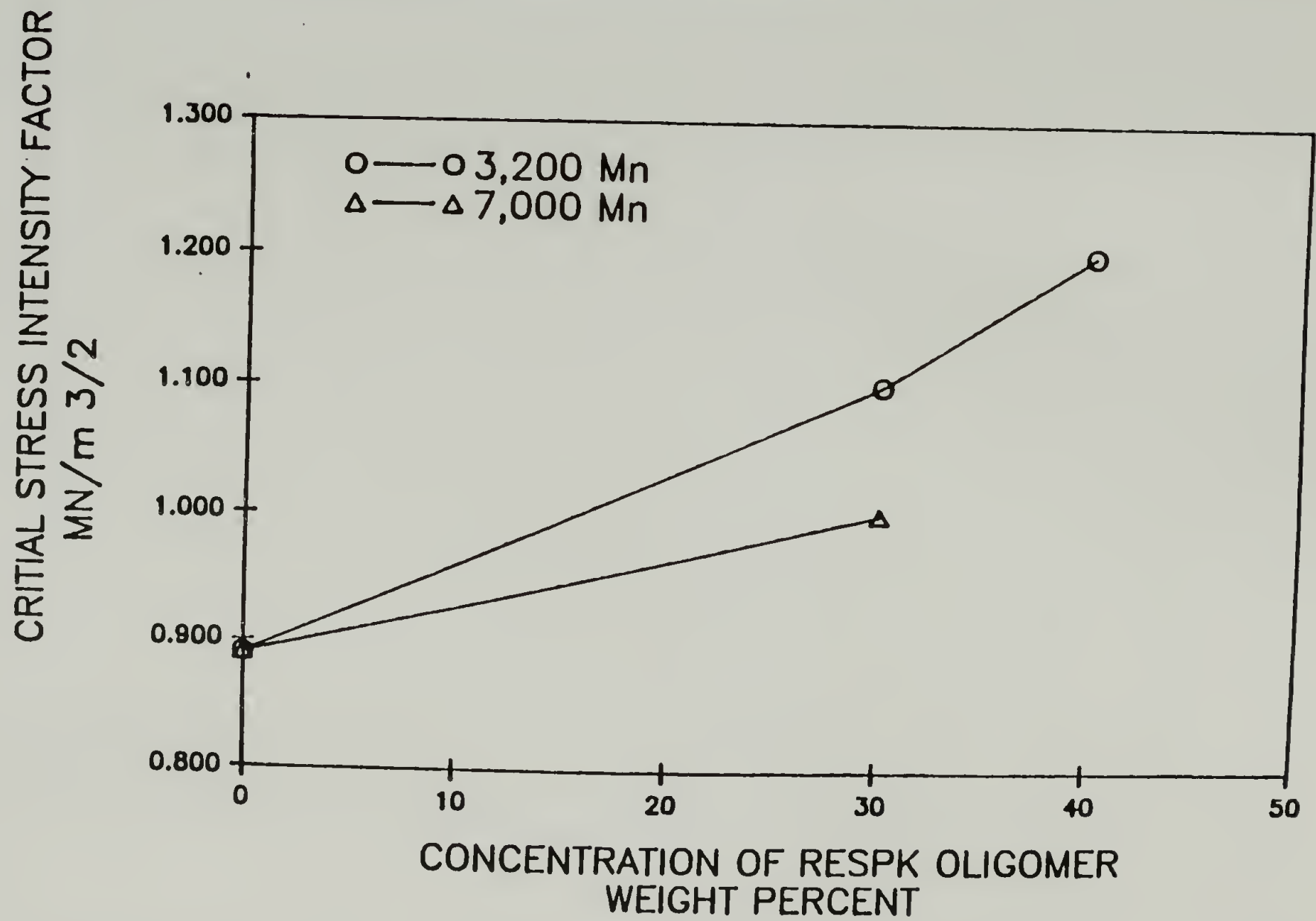


Figure 6.3 Critical stress Intensity Factor vs. Concentration of 3,400 Mn and 7,000 Mn RESPKs in Epon 828 cured with DDS at an A/E of 1.0.

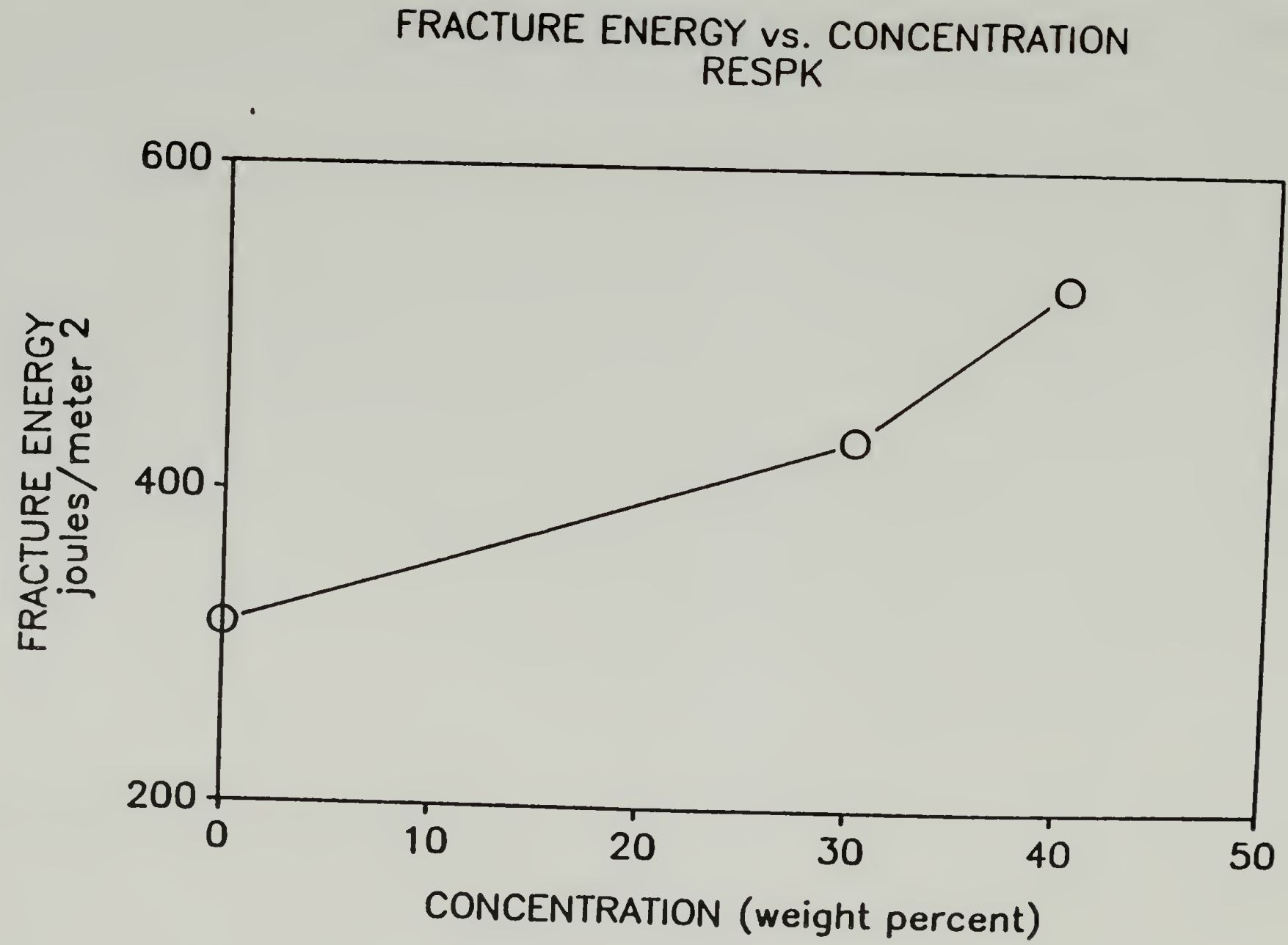


Figure 6.4 Fracture Energy vs. Concentration of 3,400 Mn and 7,000 Mn RESPKs in Epon 828 cured with DDS at an A/E of 1.0.

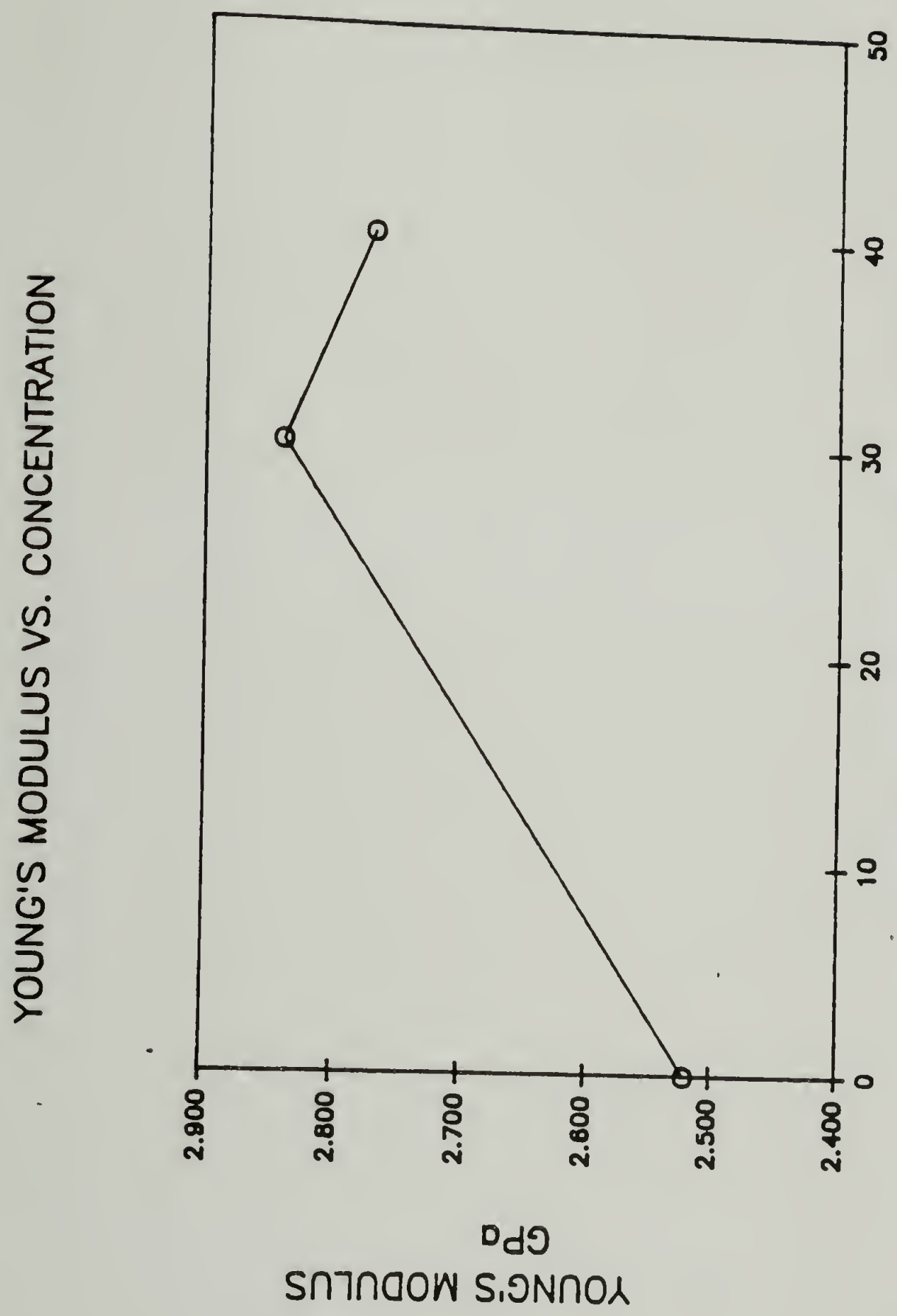


Figure 6.5 Young's Modulus vs. Concentration of 3,400 Mn RESPK in Epon 828 cured with DDS at an A/E = 1.0.

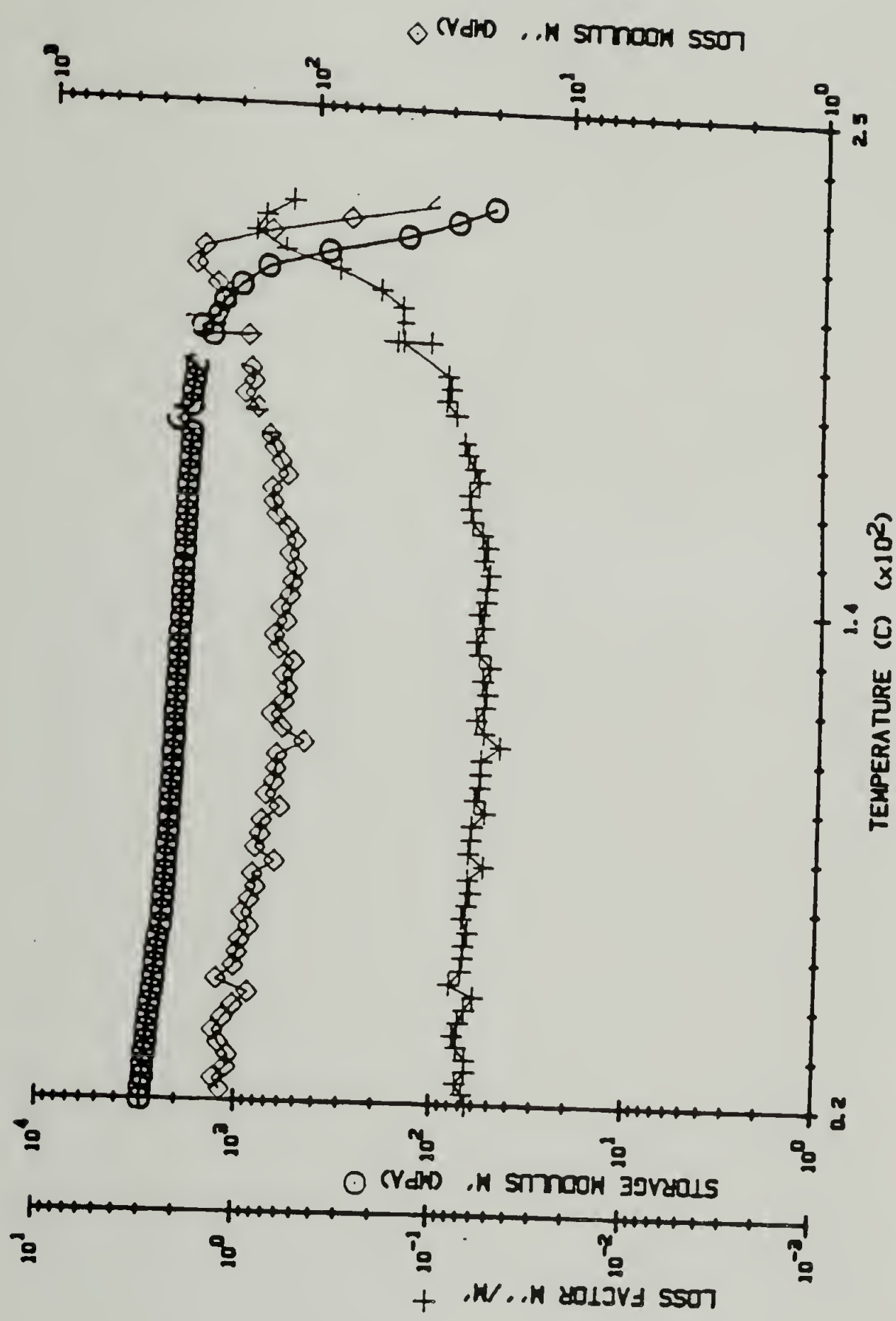


Figure 6.6 Dynamic Mechanical Properties of Epon 828/ DDS/ A/E = 1.0.

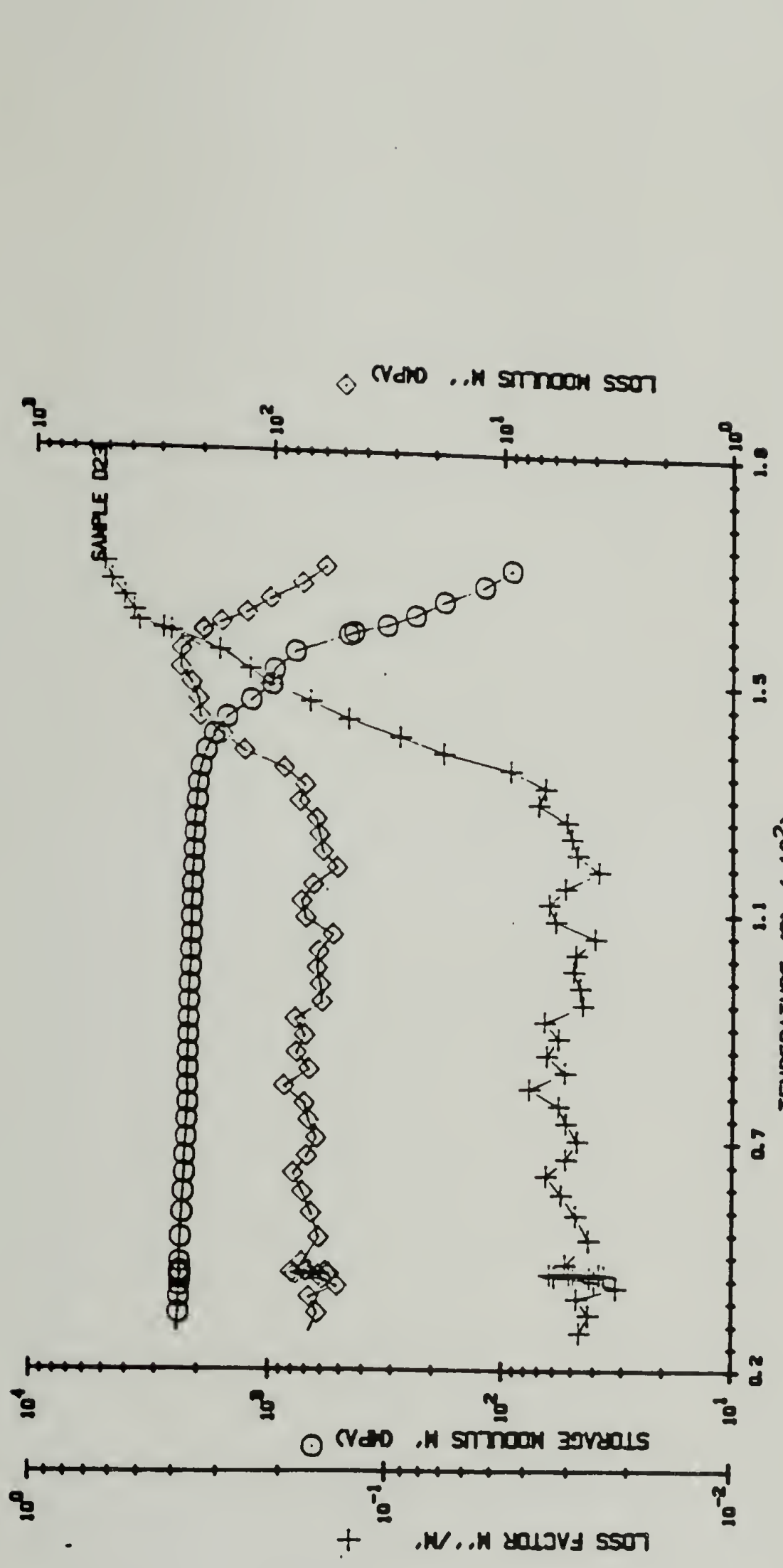


Figure 6.7 Dynamic Mechanical Properties of Epon 828/ DDS/ 40% 3,400 Mn RESPK/ A/E = 1.0.

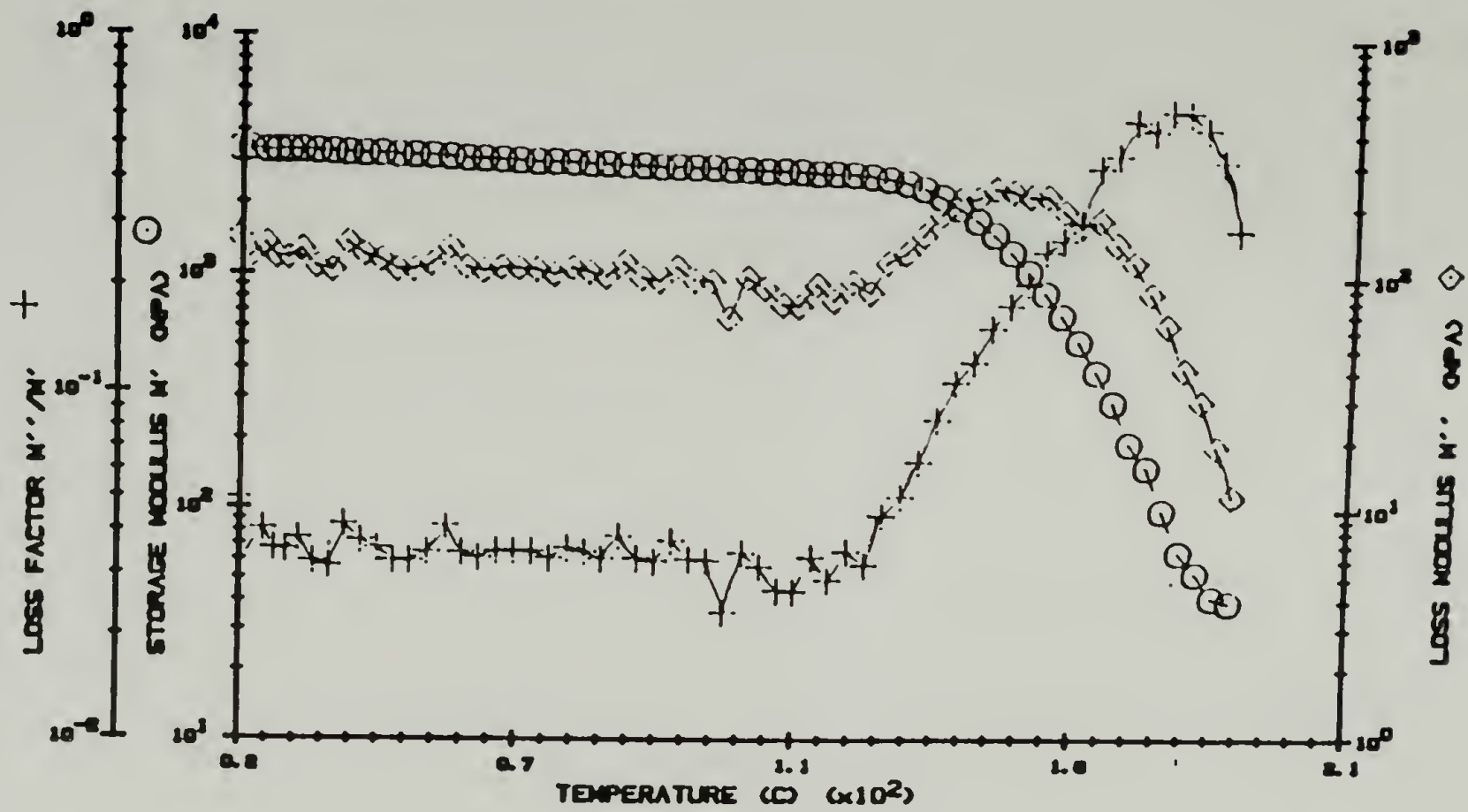


Figure 6.8 Dynamic Mechanical Properties of Epon 828/ DDS/ 30% 3,400 Mn RESPK/ A/E = 1.0.

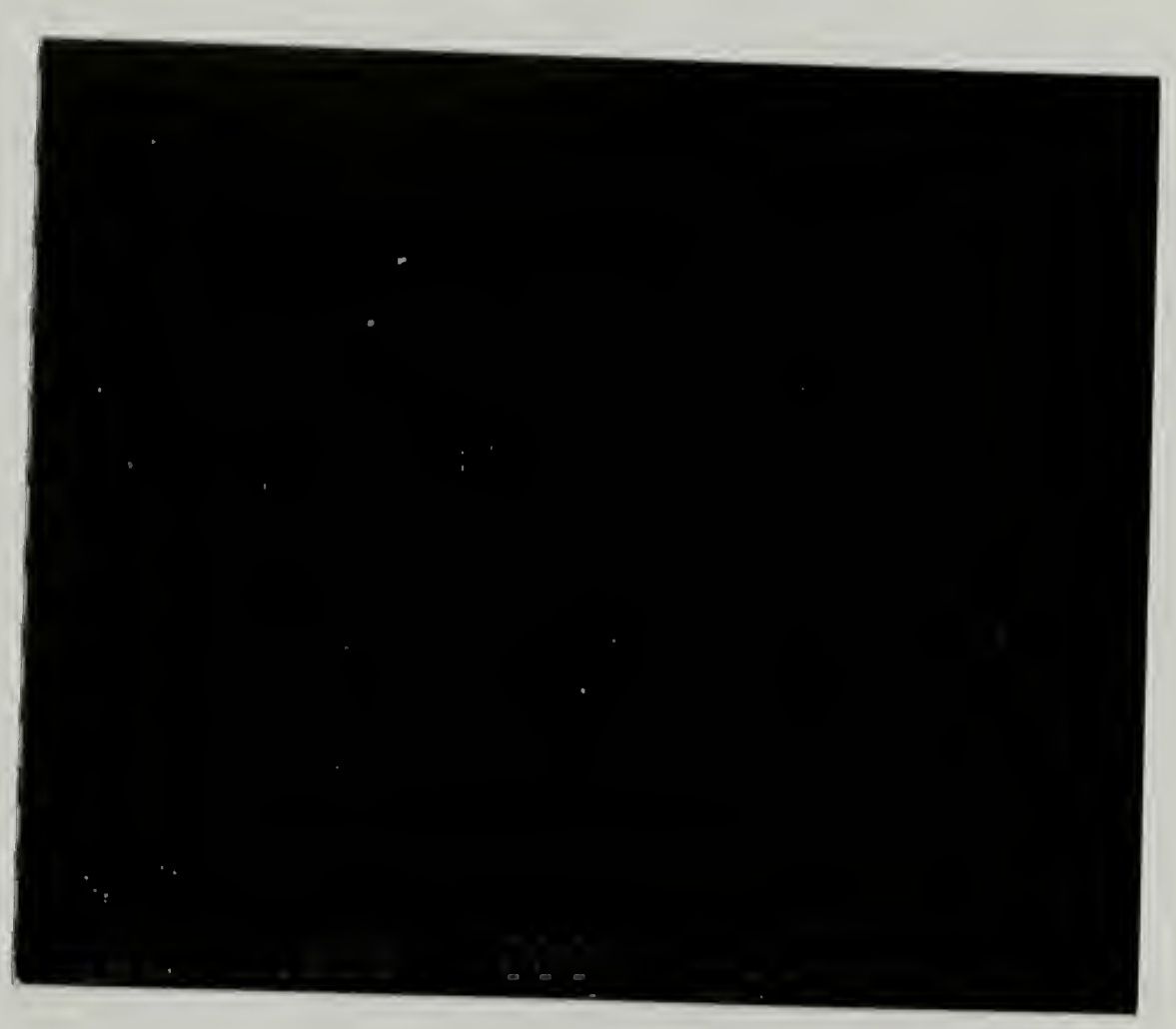


Figure 6.9 Scanning Electron Micrograph of the fracture surface of Epon 828/ DDS/ A/E = 1.0.

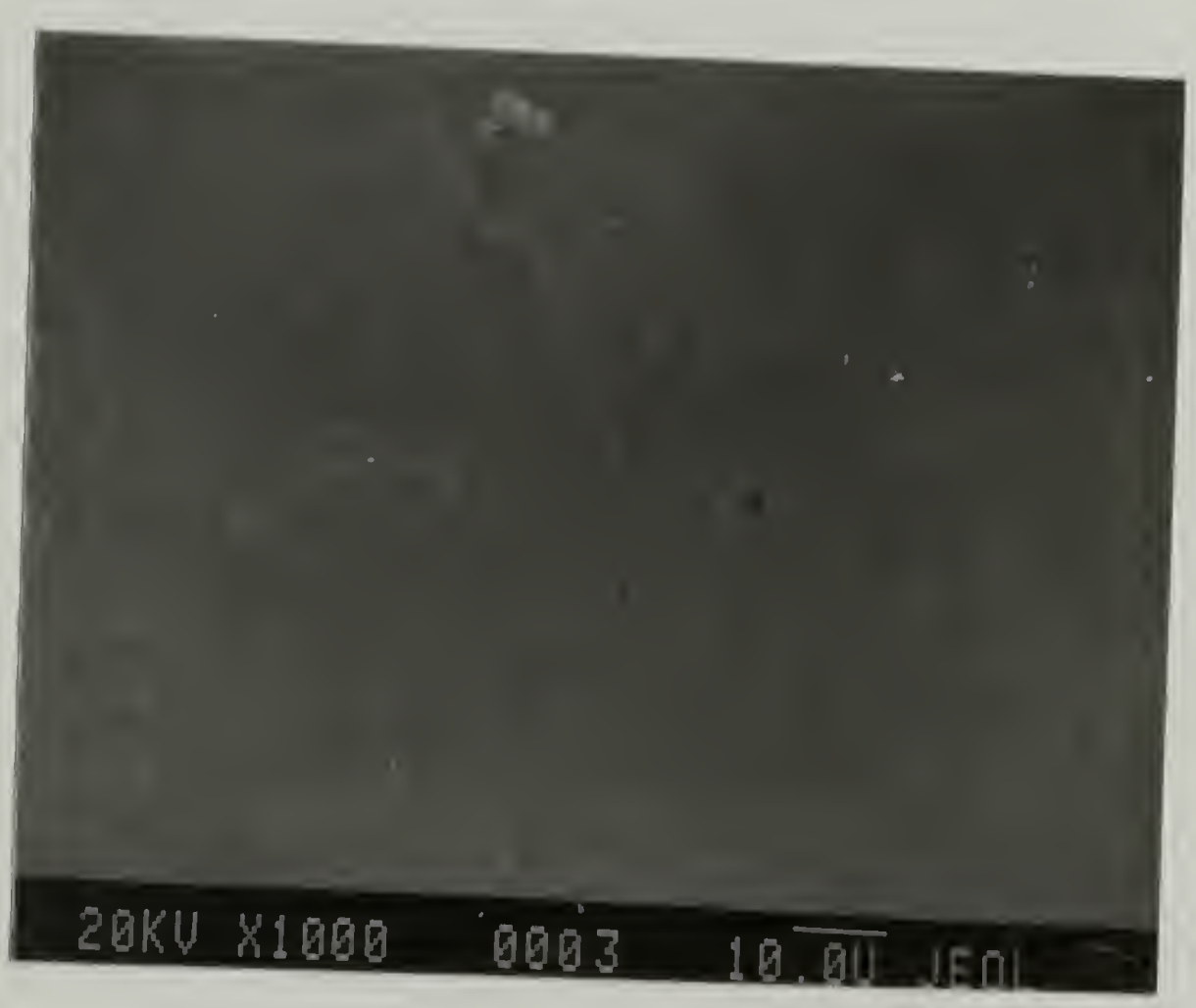


Figure 6.10 Scanning Electron Micrograph of the fracture surface of Epon 828/ DDS/ 40% 3,400 Mn RESPK/ A/E = 1.0.

as low as 155°C in the formulations with the highest levels of functionalized oligomer. Two glass transitions appear in the dynamic mechanical spectra. The drop in stiffness at the first is much less than that at the second.

In figures 6.9 and 6.10, the scanning electron micrographs of fracture surfaces are represented. Figure 6.10 represents the Epon 828/ DDS neat resin having a fracture energy of 315 J/M^2 while Figure 6.11. represents the Epon 828/ DDS/ 40% 3,400 Mn RESPK formulation having a fracture energy of 529 J/M^2. Both micrographs appear featureless at the 1000X magnification.

6.4 Conclusions

A tough matrix material cannot be achieved via the incorporation of an oligomeric end functionalized resorcinol polyetheretherketone in Epon 828 while maintaining processability. Higher molecular weight functionalized oligomers do not yield higher K_{Ic} values. The insubstantial increase in resistance to fracture makes these materials very unattractive for composite use. The lack of improvement in the fracture energy may be the result of insufficient reaction of the RESPK with the Epon 828, leading to many uncrosslinked RESPK chains. It was observed during the resin formulation process that the RESPK seemed to dissolve nicely into the Epon 828 at both of the molecular weights investigated however the resulting

mixtures were not transparent. The mixtures were opaque and light tan in appearance. This may be a good indication that the oligomer was not miscible with the Epon 828 at the very beginning (49). While it may have been immiscible there was no macroscopic phase separation. If the RESPK was immiscible with the Epon 828 a restriction on the number of reactions between these two materials would occur. There is no doubt that some reaction did occur between the two materials since controls run with RESPK containing no amine functionality at 30 and 40% loading levels were too brittle to test. If a phase inverted morphology were to develop, the 7,000 Mn oligomer is at too low of a molecular weight to have appreciable strength without linkage via epoxide groups. It is thought that these materials behave similarly to the amine terminated polyethersulphone (ATPEES) systems where at low percent incorporations the phase separated morphology consists of an epoxy matrix with ATPEES rich inclusions and at high percent incorporations the matrix is ATPEES rich and the inclusions are epoxy rich (23-26). Unfortunately TEM evidence for this phase separation process in the RESPK system is not available. In the RESPK systems at the lower loading levels the cured resin probably consists of RESPK rich inclusions in an epoxy/curing agent rich matrix. In this situation the RESPK rich inclusions should act as stress concentrators in the matrix. These stress concentrations should be small as a result of the similarity in tensile, shear, and bulk moduli in the two

phases. These small stress concentrations may cause the initiation of more localized shear yielding in the matrix resulting in an increase in the resistance to crack propagation, however a significant increase is not observed. These inclusions should also have the ability to deform in a ductile manner thereby further increasing the energy required for crack propagation. At the higher loading levels there is probably a phase inversion in which the inclusions are now epoxy/curing agent rich and the matrix is RESPK rich. In this morphology the distance between crosslinks in the matrix is greatly increased, allowing for the chain mobility required for large energy absorbing deformations. Therefore at these high loading levels the inherent level of ductility of the material should be greatly increased. Deformations should become similar to those found in the parent aromatic thermoplastic material. Unfortunately this is not the case. The lack of initial miscibility between the Epon 828 and RESPK oligomer, limiting reaction at oligomer chain ends is probably the cause of the lack of improvement in fracture resistance.

In conclusion, while the RESPK did not result in a matrix formulation with improved fracture resistance it is not an indication of the failure of this technique to improve toughness since the initial miscibility of the formulations is in question. If the miscibility between the RESPK oligomer and an epoxy resin could be improved such that reaction between the amine end groups and the epoxide

groups would occur to a greater extent a tough matrix formulation would be produced.

CHAPTER 7

CROSSLINKING OF HYDROQUINONE BASED POLYARYLETHERKETONE USING SHORT, STIFF, DIIMINE CROSSLINKS

7.1 Introduction

The demand for tough high temperature, low density materials has greatly increased in recent years. These materials are sought as replacements for metals in structural applications where specific strength and specific stiffness are of great importance (50). Areas of high demand include the aerospace and transportation industries, where cost is often a secondary concern. Many polymeric materials have been developed which have achieved substantial improvement over metals. One such polymer is the polyaryletherketone based upon hydroquinone and 4,4'-difluorobenzophenone produced by ICI Inc. This semicrystalline material is of great commercial importance as a result of its excellent mechanical properties. Hydroquinone Polyetheretherketone (HDQPEEK) exhibits excellent toughness, stiffness and resistance to most solvents (41,42). While this material boasts a melting point of 335°C there is a substantial loss in stiffness at the glass transition temperature of 143°C along with an increased tendency to creep (48). This drop in modulus is of grave concern to those seeking a material for higher temperature applications. In an effort to reduce the temperature effect upon the mechanical properties a novel

synthetic technique has been developed to provide sites for short, stiff, crosslink formation along the HDQPEEK molecular backbone. The approach taken here is novel in that it is the first to utilize the carbonyl functionality of the polymer backbone in the formation of short chain di-imine crosslinks via an aromatic diamine. This reaction between an aromatic amine and a carbonyl group was also observed by McGrath et. al when amine functionalized bisphenol A polyetherketone was molded above 220° C forming a lightly crosslinked network (51). Other methods for crosslinking HDQPEEK have been developed. In fact it has been observed that HDQPEEK crosslinks upon heating above 400° C, however the rate of this crosslinking reaction is too slow to be economically viable. Sasuga and Hagiwara have investigated the potential for electron beam irradiation crosslinking (52). Their data suggests that chain scission accompanies the crosslinking reactions. An increase in the glass transition and a decrease in the melt temperature are observed. Small increases in the shear storage modulus above the glass transition temperature were detected. Researches at Raychem have developed a method for crosslinking HDQPEEK using elemental-sulfur(53,54). Again chain scission is observed along with crosslinking. Increased modulus and strain at break at 200° C are reported as well as improved high temperature creep resistance.

7.2 Experimental

Reagents: 1,4-phenylenediamine and phenylsulphone were used as received from Aldrich Chem. Co.. HDQPEEK of approximately 16,000 number average molecular weight and a polydispersity of 2 was used as received from ICI Inc.

Synthesis: A 4 neck 250ml round bottom flask was equipped with a stirrer, thermometer, nitrogen inlet and outlet and a heating mantle. HDQPEEK (5gr), 1,4-phenylenediamine (20gr) and phenylsulphone (80gr), were weighed into the flask. The diamine is at a ten times excess with respect to carbonyl and endgroups to minimize crosslinking in solution. The flask was continuously purged with dry nitrogen. The system was heated to 270° C to effect a complete solution then cooled to 230C + 10° C. This temperature was maintained for 3 hours. The system was then cooled to 125° C at which point the contents of the flask were transferred to a crystallization dish. After cooling to room temperature, the now solid reaction mixture was broken into small pieces and dispersed into 500mls of acetone. The phenylsulphone and excess 1,4-phenylenediamine dissolve leaving a rubbery percipitate. This precipitate was further washed with acetone. A thin film (.08mm) was pressed from this acetone swollen rubbery precipitate. The film was heated at 200° C for 1 hour under pressure to remove residual acetone and give the film sufficient mechanical integrity for handling.

Mechanical Properties: Tensile samples were cut from the amine functionalized HDQPEEK (AFHDQPEEK). Dynamic mechanical properties of these film samples were characterized as a function of temperature and time using a Dynastat dynamic mechanical tester from IMASS Inc. (appendix D). For comparison samples of HDQPEEK were also characterized. Differential Scanning Calorimetry and Thermogravimetric Analysis measurements were also made on these films at a heating rate of 20°C/min on Perkin Elmer DSC II units.

7.3 Results and Discussion

The reaction of the diamine with the HDQPEEK occurs at the carbonyl linkages along the polymer backbone leading to the formation of hemiaminals which eliminate water to form imine linkages (44) as shown in Figure 7.1.. Upon further heating of this material unreacted amine reacts with unreacted carbonyl to give imine crosslinks with the elimination of a second molecule of water. In Figures 7.2. through 7.4. the dynamic tensile storage modulus is plotted against temperature for commercial HDQPEEK, uncured AFHDQPEEK and cured AFHDQPEEK. In Figure 7.2. commercial HDQPEEK is represented. This sample was annealed to obtain maximum crystallinity prior to the temperature sweep. Even with the high level of crystallinity a sharp drop in E′ is

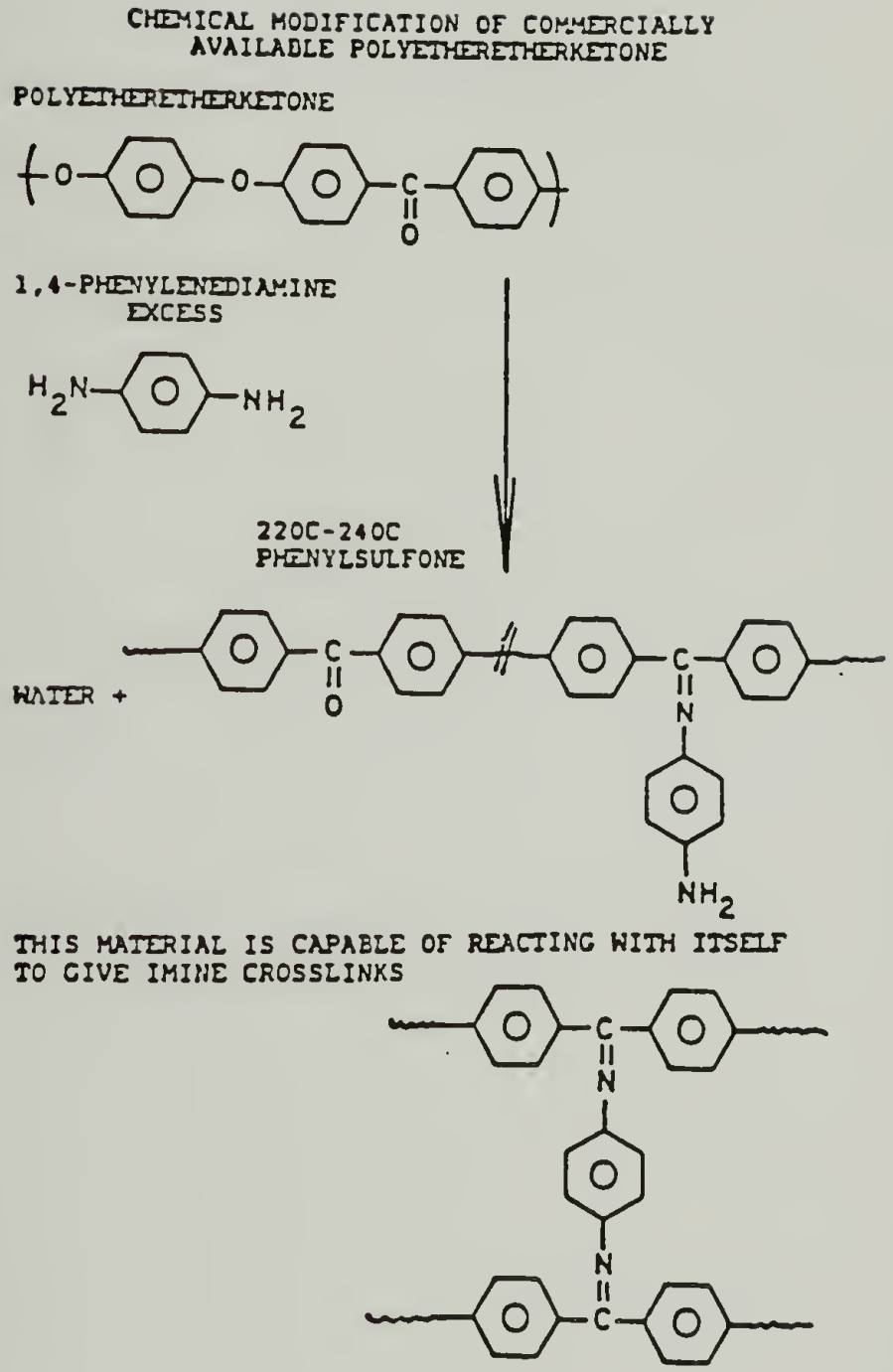


Figure 7.1 Reaction Scheme for chemical modification of commercially available polyetheretherketone.

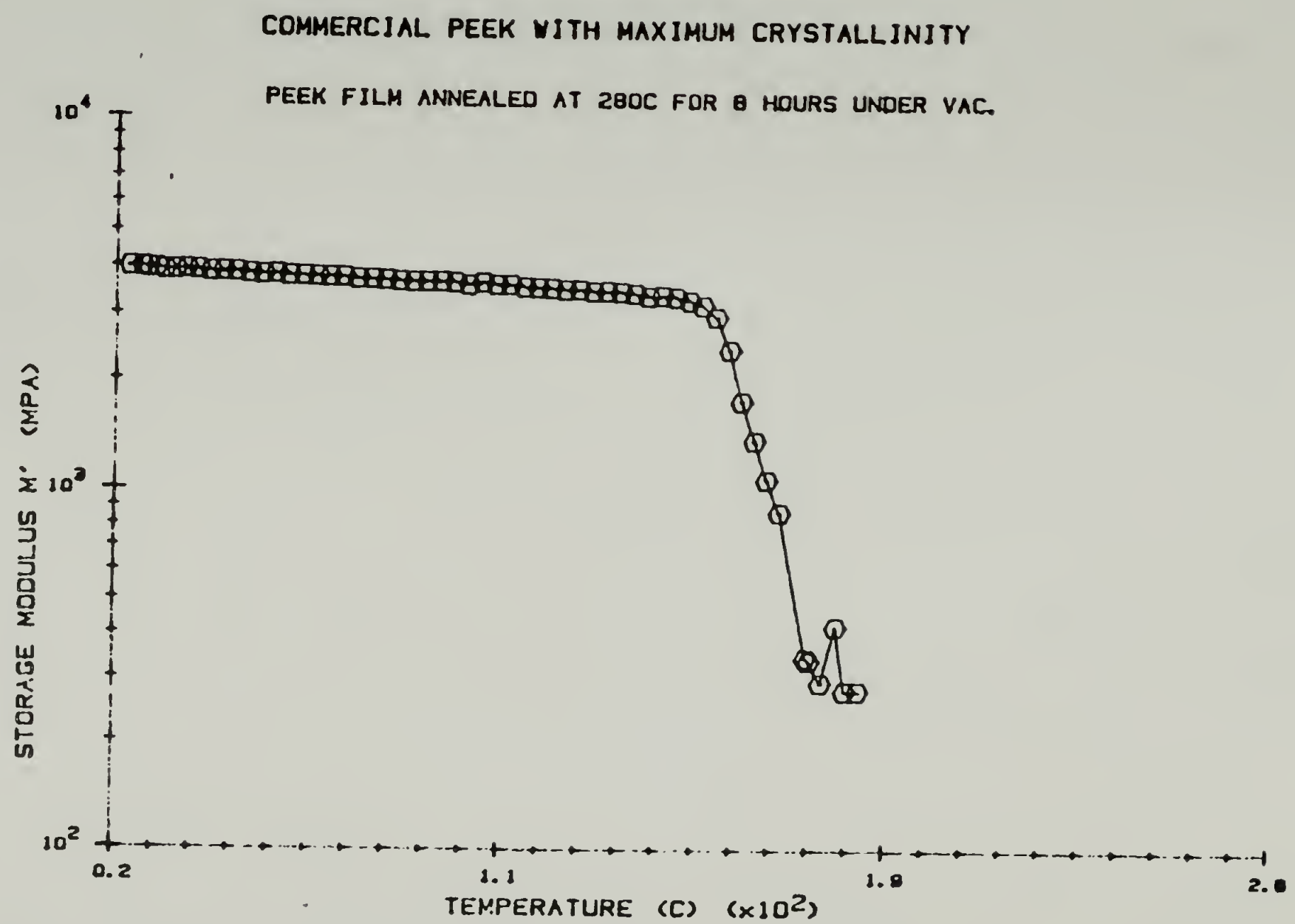


Figure 7.2 Dynamic Mechanical tensile storage modulus vs. temperature for commercial PEEK.

observed at 150° C to a level of 200 Mpa. In Figure 7.3., the uncured AFHDQPEEK shows an even larger drop in E' 30° C below that of the starting material to a level of 10 Mpa. This figure also shows a large increase in E' at 200° C during isothermal cure in the Dynastat temperature chamber at 200° C. The actual time at 200° C is 3 hours, during which E' climbs from 10 Mpa to 2 Gpa. Upon isothermal heating of commercial HDQPEEK at 200° C no such increase is observed. Figure 7.4. is a plot of E' vs. temperature up to 280° C for the film used in Figure 7.3.. This figure shows no drop in E' which can be associated with a glass transition temperature below 280° C. Therefore a material which was originally a soft rubber at 280° C is now a stiff glass at this temperature. A large dependence of cure time on film thickness was observed in this AFHDQPEEK as a result of the dependence of the crosslinking reaction on water removal.

Thermogravimetric Analysis (TGA) data for commercial HDQPEEK and cured AFHDQPEEK is shown in Figure 7.5.. The two materials behave quite similarly with no weight loss until 600° C and 630° C respectively. The thermal degradation curves parallel each other with the cured AFHDQPEEK losing 10% less than commercial PEEK at 800° C. TGA of uncured AFHDQPEEK shows significant weight loss at the cure temperature of 200° C due to the evolution of water of reaction.

Differential Scanning Calorimeter (DSC) data for commercial HDQPEEK, uncured AFHDQPEEK and cured AFHDQPEEK is

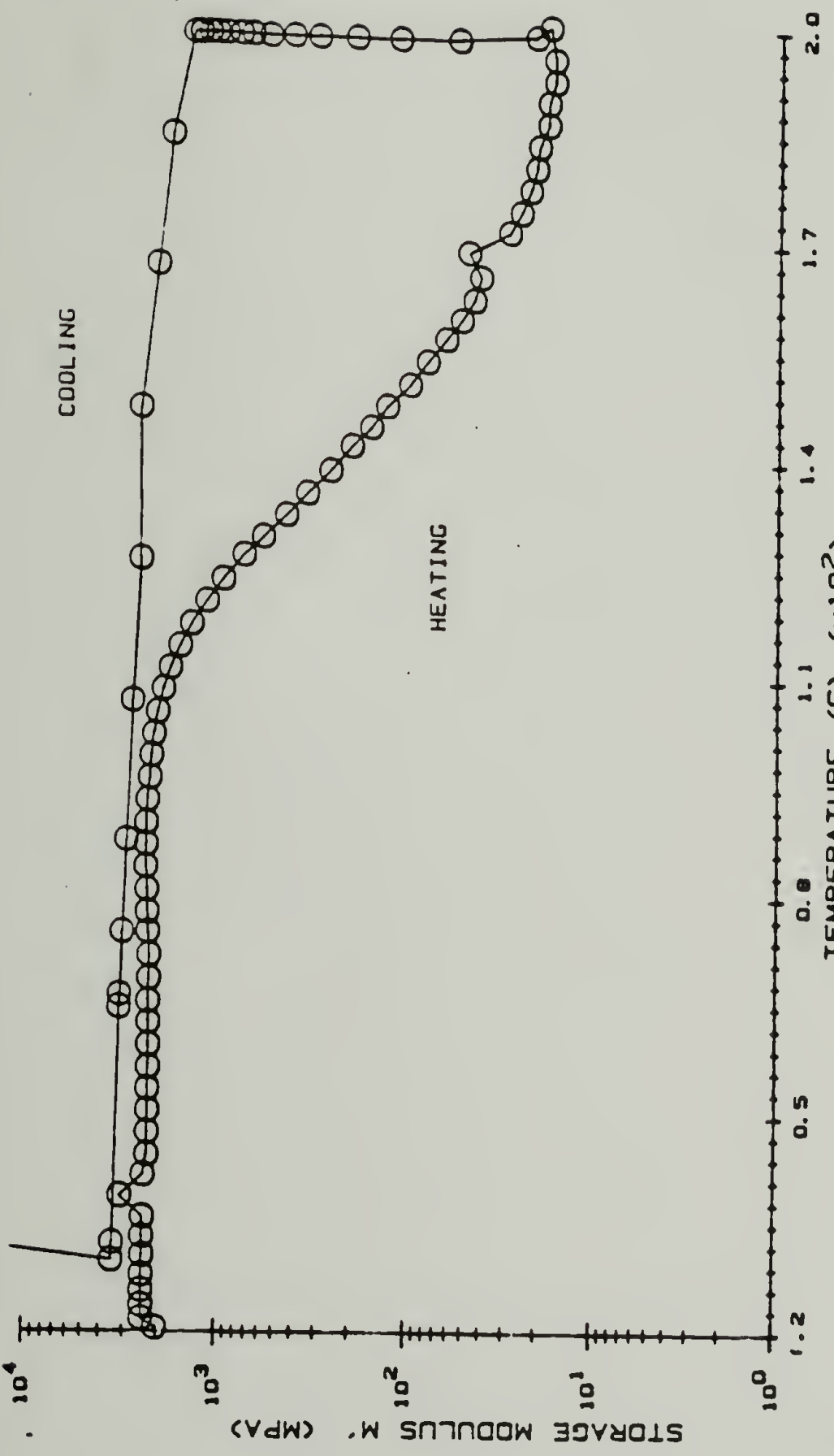


Figure 7.3 Dynamic Mechanical tensile storage modulus vs. temperature for amine functionalised commercial PEEK.

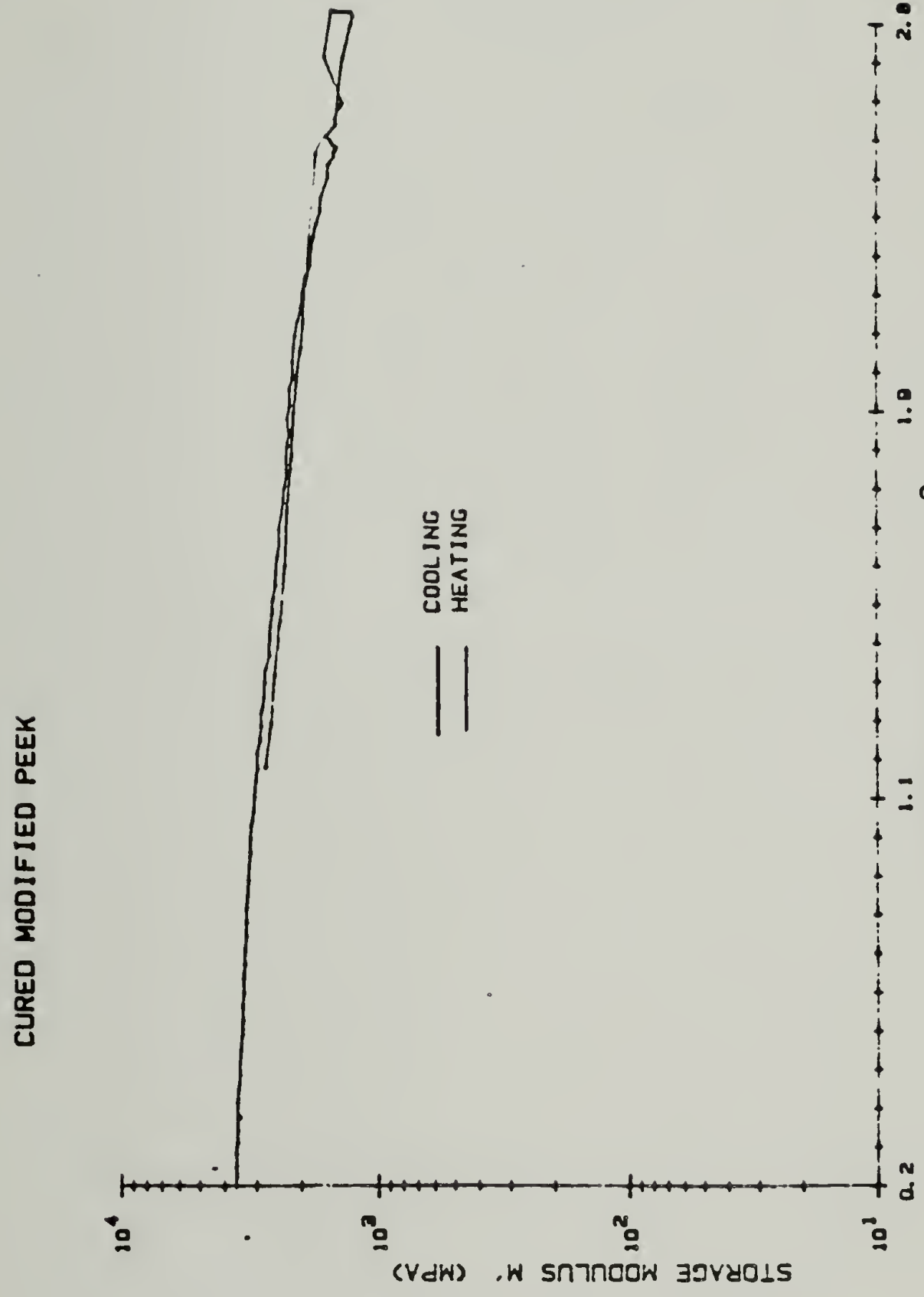


Figure 7.4 Dynamic Mechanical tensile storage modulus vs. temperature for cured amine functionalised commercial PEEK.

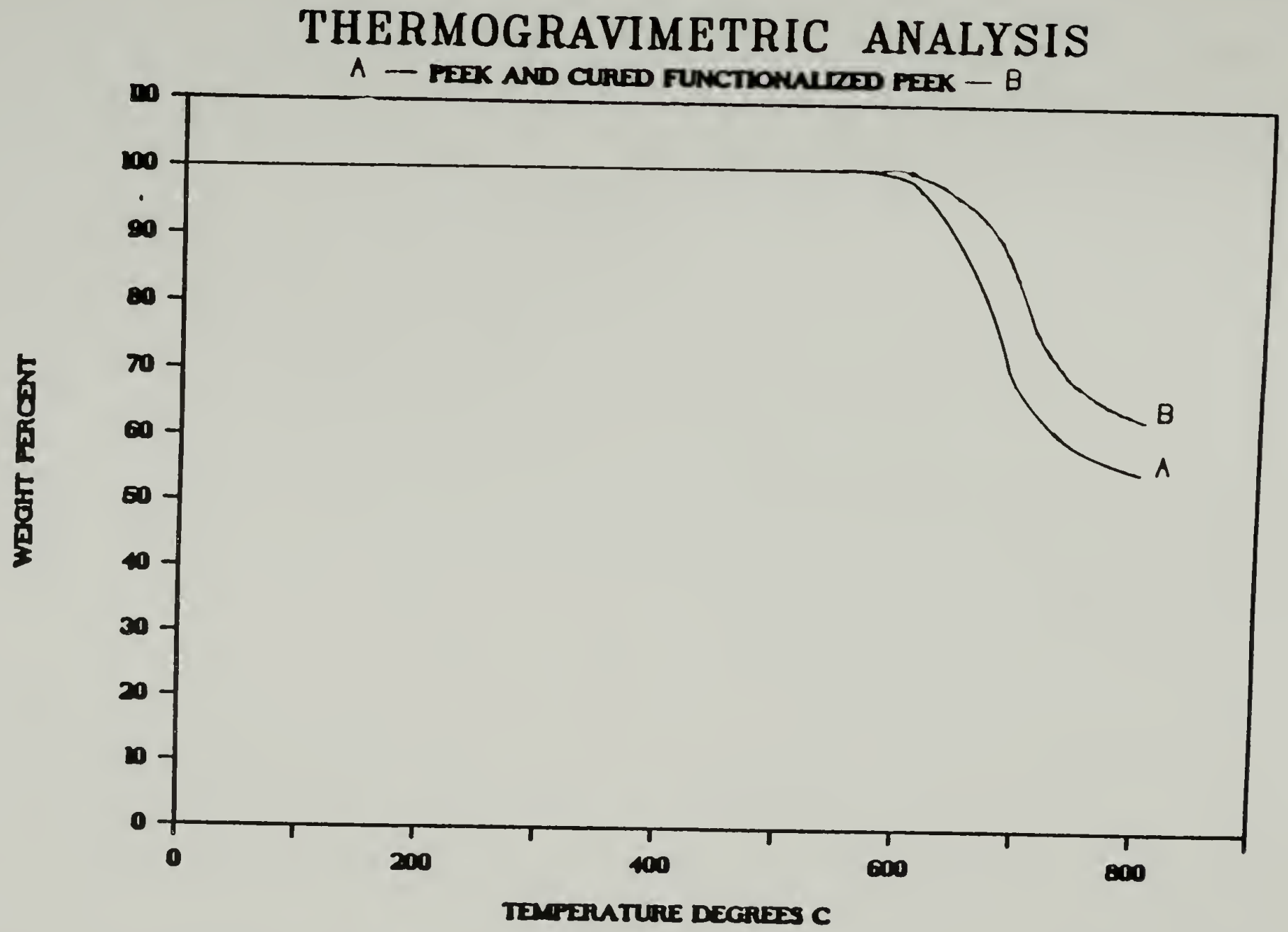


Figure 7.5 Thermogravimetric Analysis of commercial PEEK and cured amine functionalised PEEK.

shown in Figures 7.6. through 7.8.. The scan for HDQPEEK shows the double melting peaks typical of this material (55,56). The DSC scan for the uncured AFHDQPEEK shows no melt transition, however there may be one large endotherm due to volatization of water of reaction. The data on the cured AFHDQPEEK shows a single melting peak in the HDQPEEK doublet.

Solubility studies have revealed that cured AFHDQPEEK is swollen by, but insoluble in methane sulfonic acid despite the solubility of HDQPEEK.

Elemental analysis of the uncured AFHDQPEEK shows an increase in the nitrogen content over HDQPEEK of 6.6%. Nucleophillic aromatic substitution of the diamine for the fluorine end groups accounts for .1%, with the remaining 6.5% suggesting replacement of 2/3 of the carbonyl groups with imine groups.

Carbon 13 NMR data for the cured AFHDQPEEK is shown in Figures 7.9. and 7.10.. The spectrum for the cured AFHDQPEEK shows the absence of the carbonyl absorbance at 192 ppm which is clearly present in the HDQPEEK spectrum, and the presence of the imine absorbance at 156 ppm.

7.4 Conclusions

From the data it can be concluded that the observed increase in E' upon curing at 200°C and the lack of solubility of the cured AFHDQPEEK strongly support crosslink

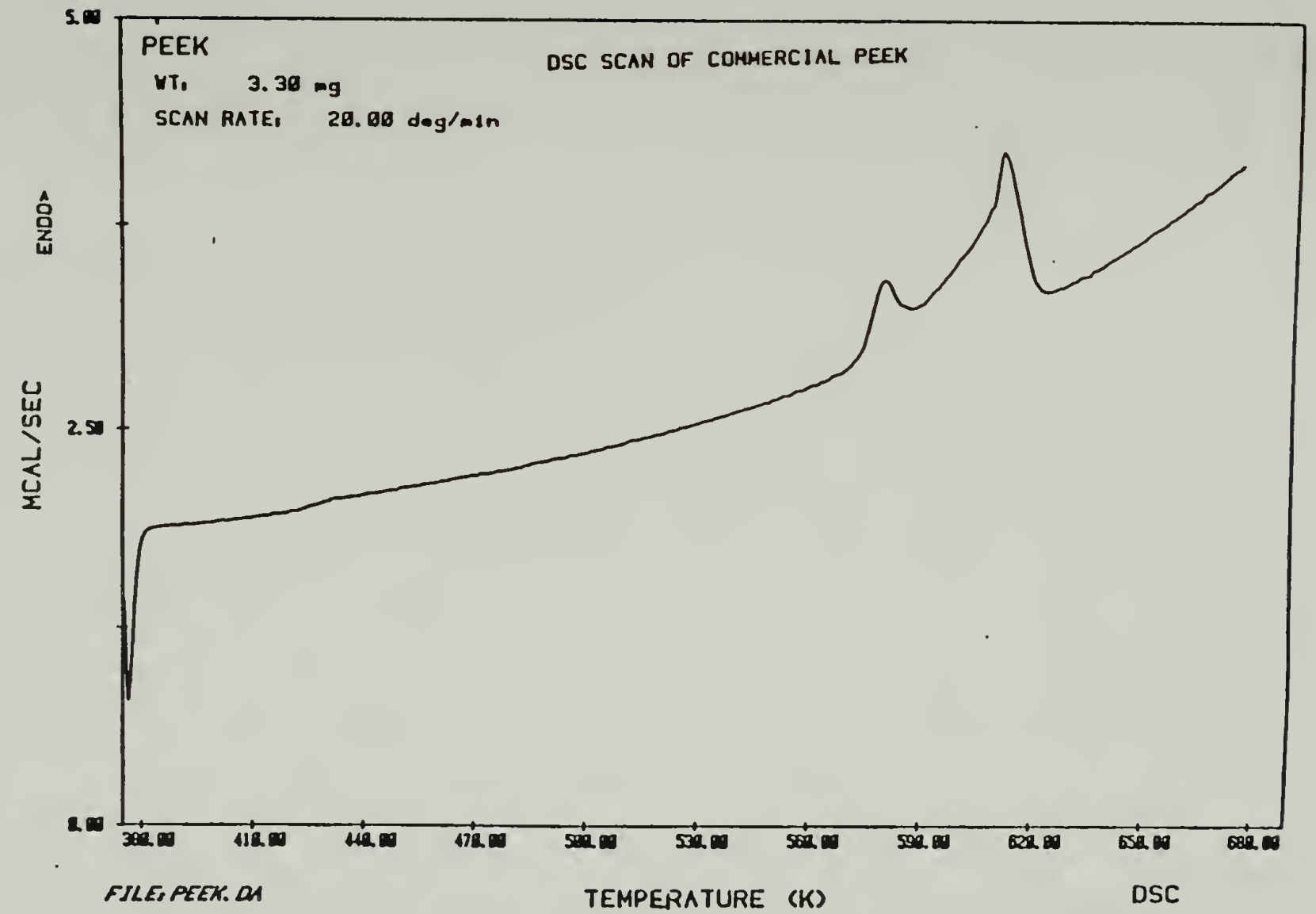


Figure 7.6 Differential Scanning Calorimeter scan of Commercial PEEK.

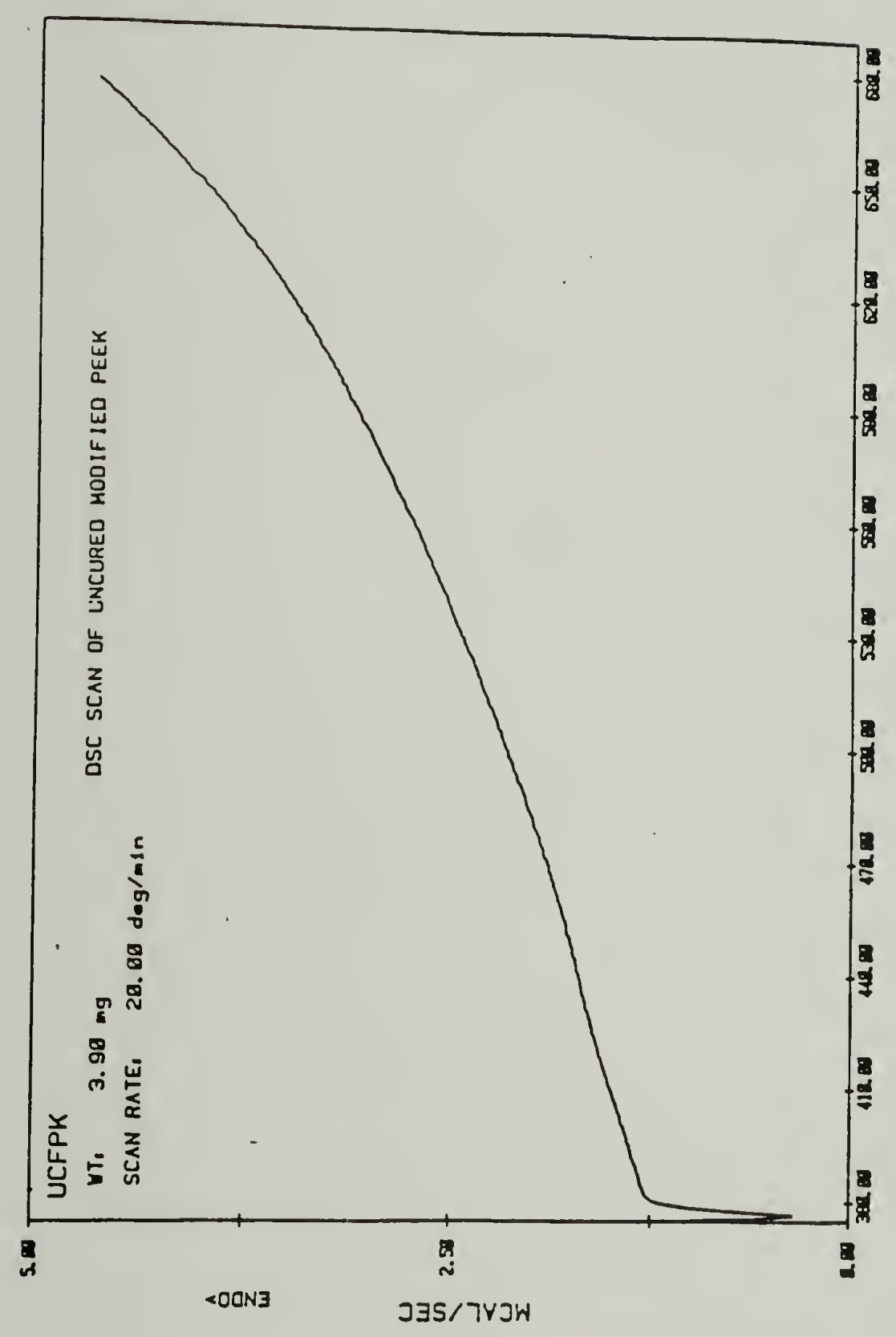


Figure 7.7 Differential Scanning Calorimeter scan of uncured amine functionalised PEEK.

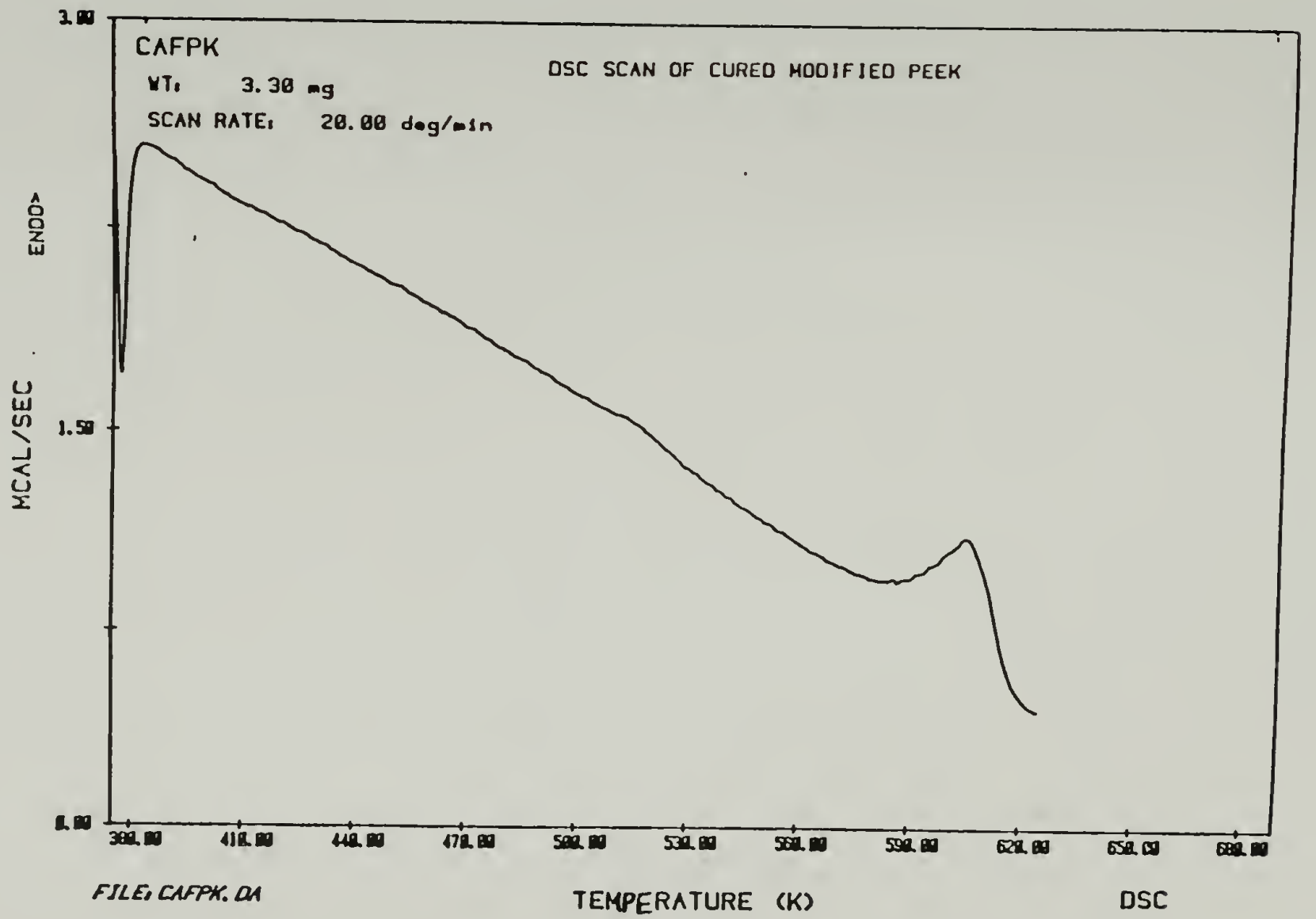


Figure 7.8 Differential Scanning Calorimeter scan of cured amine functionalised PEEK.

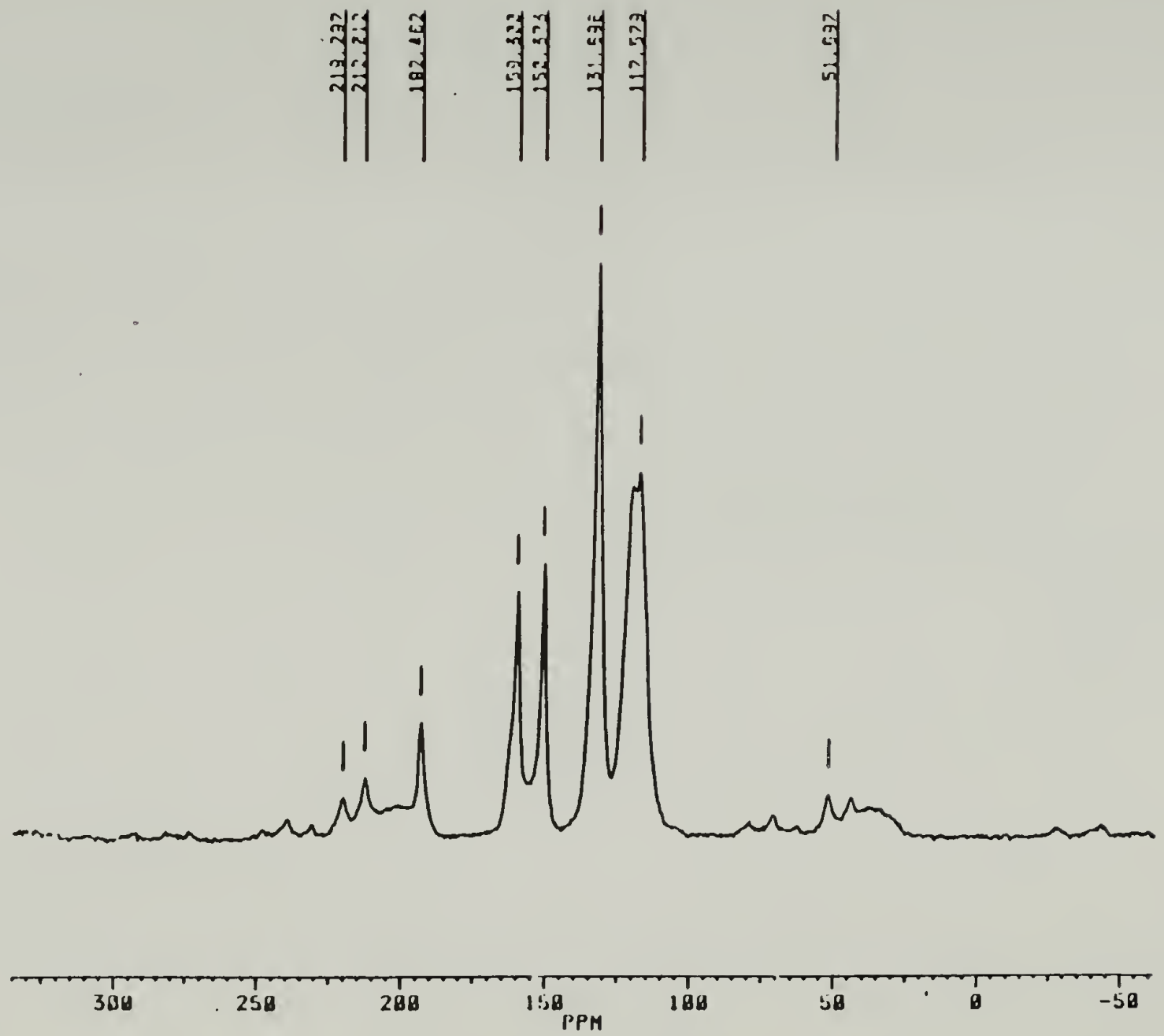


Figure 7.9 Carbon^{13} NMR spectrum of commercial PEEK.

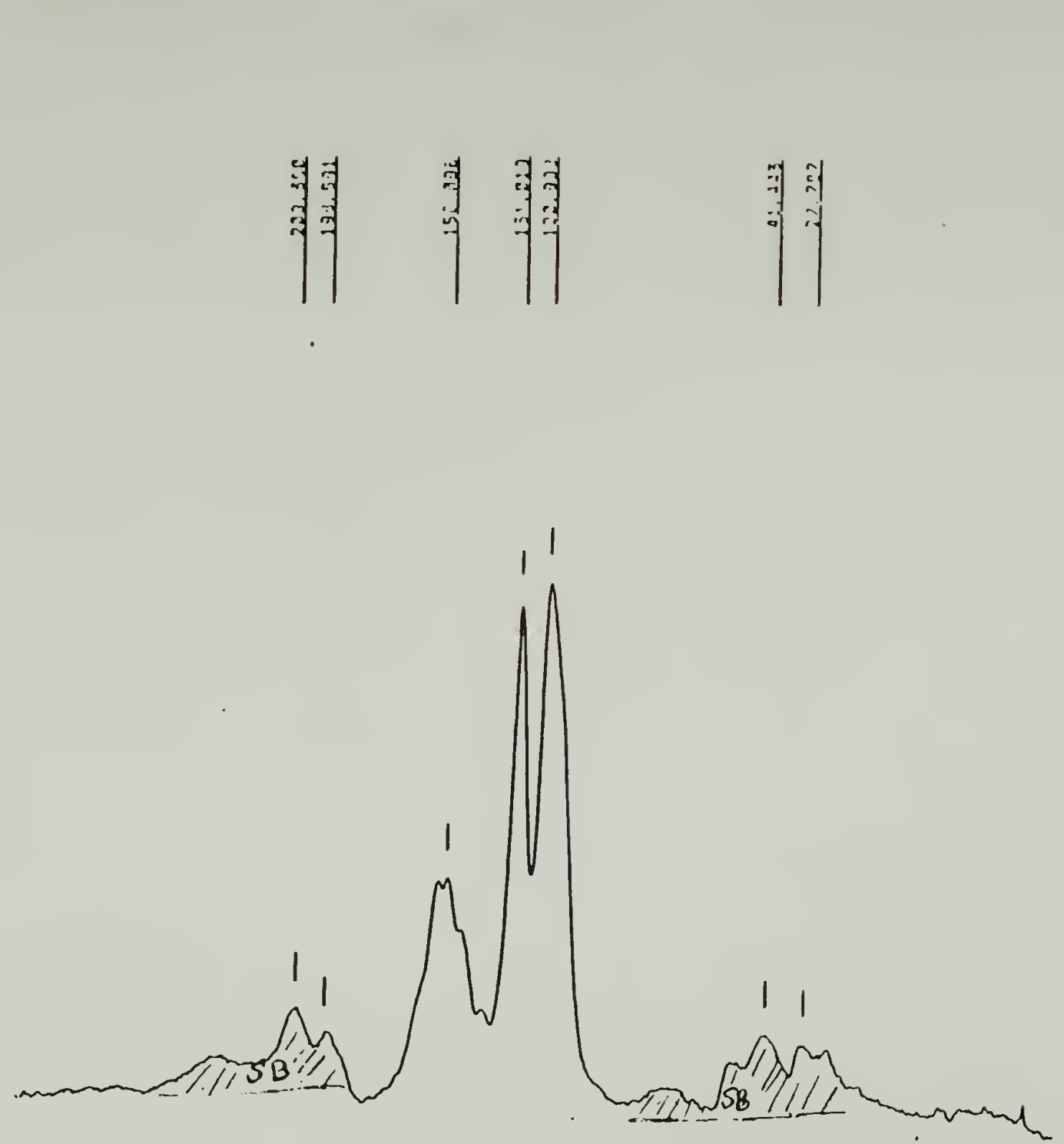


Figure 7.10 Carbon^{13} NMR spectrum of cured amine functionalised PEEK.

formation but alone do not confirm it. The dependence of cure time upon film thickness, elemental analysis data, weight loss of the uncured film at the cure temperature and the endotherm above 100°C in the DSC scan of the uncured AFHDQPEEK also support the imine formation mechanism. The carbon 13 NMR spectra have shown conclusively that the AFHDQPEEK crosslinks via an imine formation reaction with the evolution of water.

Since crosslinking is occurring through reaction at the carbonyl groups this technique could be utilized on many ketone containing polymers. Polymers containing benzophenone linkages are the most likely candidates as a result of the inherent stability of the Schiff bases formed. Polymers with aliphatic ketones would be much more sensitive to hydrolysis. The crosslink densities of these materials could be modulated simply by regulation of the amount of functionalisation of the polymer backbone. Through the regulation of the crosslink density a wide spectrum of mechanical properties will become available. Preliminary work has suggested potential uses for AFHDQPEEK as a molecular composite matrix with poly-p-phenylenebenzobisthiazole as well as use as an adhesive repair material for ketone containing thermoplastic composites.

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

It has been demonstrated that extremely fracture resistant resin formulations can be produced by coreacting amorphous aromatic amine functionalised polyaryletherketones, low molecular weight diamines and commercial epoxy resins. These systems not only attain excellent toughness but also exhibit good water resistance and great ease of processing. This dissertation has also shown that the semicrystalline polyaryletherketones investigated cannot be used in this application as a result of the high incorporation temperatures. When lower melting oligomers were used it was discovered that crystallinity did not develop in the PEEK rich phase. In fact crystalline particles added to the epoxy system were observed to melt well below the crystalline melt temperature while remaining particulate in nature. Melting presumably occurred due to swelling by the epoxy resin.

In developing and characterizing these materials an improved understanding of the mechanism by which these systems work has been developed. The Transmission Electron Microscopy data clearly indicates phase separation at the higher loading levels into a polyaryletherketone rich continuous phase with epoxy rich inclusions. In this morphology the level of fracture resistance approaches that of high molecular weight polyaryletherketone homopolymer.

The Scanning Electron Microscopy data from the fracture surfaces of these systems indicates that the increase in fracture resistance is due to a large increase in deformation of the material in the fracture plane during failure. This increased deformation, or tearing, of the fracture plane requires increased energy input prior to catastrophic failure.

This work has also demonstrated the need for covalent bonding between the polyaryletherketone and the epoxy resin in the phase inverted morphology. Without this chemical bond the molecular weight of the oligomers used is insufficient for the attainment of significant improvements in mechanical behavior. The epoxy resin in this morphology is acting merely as a linkage unit, extending the polyaryletherketone chain. This extended chain is fixed into the network instead of relying solely upon molecular entanglements in the prevention of long chain disengagement.

The need for covalent bonding between the phases at the lower loading levels where the continuous phase is epoxy rich has not been investigated. In this morphology some improvement in toughness was observed. This improvement was greater than that obtained in high glass transition temperature epoxy resins containing functionalised acrylonitrile butadiene rubbers. In both systems the modification of the state of stress in the material due to the presence of the phase separated inclusions would be expected to be similar. Therefore the improvements in

fracture resistance in this morphology are probably not the result of the presence of the polyaryletherketone rich inclusions. Instead the improvements in fracture resistance are probably the result of the increased average molecular weight between crosslinks in the epoxy rich phase due to incomplete phase separation. Evidence for incomplete phase separation is seen in the lowering of the glass transition temperature for formulations having this morphology. Increased fracture resistance is then a result of the increased ability of the continuous phase to undergo molecular motion in response to critical stress levels. This molecular mobility prior to failure increases the energy absorption of the system. The rubber containing systems were designed such that complete phase separation occurs to limit the drop in modulus and the glass transition temperature of the material. If phase separation had not been so complete in the rubber containing systems greater improvements in fracture resistance would probably have been observed at the expense of material stiffness and use temperature.

Theoretically a one phase system containing a large amount of a compatible end functionalised tough aromatic thermoplastic oligomer would be capable of greatly increased fracture resistance as the average distance between crosslinks is increased. Toughness approaching that of the homopolymer would probably not be possible as a result of the presence of molecular crosslinks in the cured system.

The two phase systems would therefore be superior in fracture toughness, and as a result of the morphology, present a better barrier to water absorption. The one phase system would however be easier to market as a result of the difficulties in controlling the reproducibility of the two phase systems as a result of the dependence of morphology upon thermal history.

As stated earlier a processable, lightly crosslinked, aromatic thermoplastic has been produced, not a toughened epoxy. In this crosslinked form not only has toughness approaching that of the homopolymer been attained but the problems of creep and fatigue failure associated with thermoplastic materials should also have been alleviated. Although experimental evidence for this improvement in fatigue and creep behavior has not been obtained it is reasonable to assume that the crosslinks will limit creep during static as well as fatigue loading at subcritical loads.

8.0.1 Summary

This dissertation has helped to understand the mechanism by which the improved mechanical properties of these amine functionalized polyaryletherketone containing formulations is attained. In reaching this goal novel formulations having superior fracture resistance to any high glass transition temperature thermoset systems currently on

the market have been developed. Unfortunately this dissertation have also succeeded in uncovering many more questions which need to be answered. These questions will hopefully be addressed in future work.

8.0.2 Future Work

Since this technique of coreacting functionalised aromatic thermoplastic oligomers with low molecular weight aromatic diamines and epoxy resins is relatively new, much investigation remains to be done. This work and all other work reported to date has ignored the parameters involved in the phase separation process. To fully understand these systems, phase diagrams should be constructed to elucidate the kinetics and thermodynamics of the phase separation process. An investigation of the dependence of phase behavior and mechanical properties on the weight percent of the functionalised oligomer needs to be carried out in a more thorough manner. With knowledge of the dependence of mechanical properties on the incremental change in oligomer concentration a better understanding of the deformation process will be developed. With respect to the deformation process a thorough study of the dependence, if any, of fracture resistance on the compact tension sample thickness must be carried out to ascertain whether or not these materials deform via shear yielding, crazing or some combination of the two. Along these lines a dilatometric

study of volume change during deformation will help confirm the type of deformation process occurring. It would be very interesting to know if the fracture toughness criteria for plain strain does indeed give a lower bound for these materials as it does in metals. Perhaps it is plane stress which gives the lower bound to the fracture toughness in these materials.

A thorough characterization of all mechanical properties such as tensile behavior, compressive behavior and thermal expansion behavior remains to be carried out.

It also remains to be shown that these large improvements in fracture resistance in the matrix will transfer over to the composite structures. It is well known that improvements in matrix mechanical properties do not always give an equal improvement in composite mechanical properties. Fracture and impact tests must be run on carbon fiber reinforced composites manufactured from prepreg tapes of these resin formulations. This testing will require that large amounts of resin be synthesized. This synthesis will involve conquering the problems associated with scaling up a reaction of this type.

Other than the oligomers used in this study only polyetherethersulfone has been investigated in this application. Many other oligomers may work in this application provided they can be dissolved into a commercial resin. Low molecular weight liquid polyfunctional reactants other than epoxy resins may also work to produce the desired

properties. Obviously for commercial applications involving aerospace structures, higher glass transition temperature systems will always be in demand. To attain higher glass transition temperature formulations, oligomers having stiffer backbone units are required (ie. napthalene diols).

An intensive study into the effect of covalent bonding between the phases in the low weight percent loading morphology should be carried out. Such a study would answer once and for all the question of the amount of bonding required for increases in toughness to be observed. To my knowledge no such study has ever been carried out while holding all other factors such as domain size and percent loading constant.

Although synthetically more difficult, a study into the effect of the distance between covalent bonds with the epoxy resin along the oligomer backbone would help elucidate the effect of molecular weight between crosslinks on mechanical properties.

APPENDIX A
Preparation of Fracture Samples

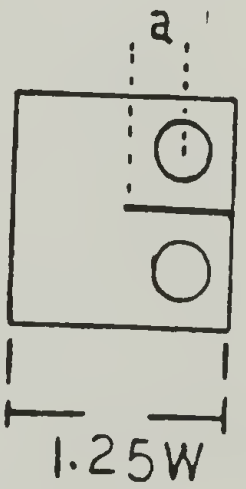
Fracture samples were cut from the 3mm sheets of cured resin using a 2.5 inch diameter jewelers slotting saw blade of .02 inches in thickness. The blade was mounted in a Bridgeport milling machine such that the blade rotation plane was perpendicular to the large surface of the 3mm sample sheet. The Bridgeport was run at 1200 revolutions per minute. No cutting fluids were used. To avoid excess heating on difficult samples a teflon mold release agent was applied to the blade to reduce friction. The sample sheets were first cut into strips of 12.0mm width. These strips were subsequently cut into 12.5 mm x 12.0mm compact tension samples and 60 mm x 12.0mm three point bend samples. The compact tension samples were then placed into a template device to align the drill for pin hole installation. A drill having a diameter of 2.50mm was used. The drill was run at 1250 revolutions per minute. The drill was slowly inserted into the sample to prevent brittle fracture. After drilling the samples, (except the HDQPK resin samples) precracks were inserted using an above Tg precrack insertion technique developed by Swetlin at the University of Akron (57). This technique involves heating the compact tension samples to a temperature 50 to 70 degrees centigrade above their glass transition temperature at which point the cured resin samples are in a soft rubbery state. In this state it is relatively easy to slice the samples with a razor blade. A special cutting apparatus is used to insure that a precrack of constant sharpness is inserted into the correct plane of the sample. For the specifics of this procedure see reference (36). The HDQPK resin formulations were prepared by using the jewelers slotting blade to insert a saw cut in the fracture plane followed by scoring with a single edged razor blade at room temperature. Sample precracks prepared in this manner are inferior to those inserted using the above Tg method. These sample precracks tend to be dull, have geometric parameters which are dependent upon sample stiffness and razor pressure. Therefore this room temperature scoring technique yields K_{Ic} values which are artificially high and contain extensive scatter. Obviously samples prepared in this manner at room temperature cannot be compared with those sliced above Tg.

APPENDIX B
Critical Stress Intensity and Fracture Energy Determinations

The critical stress intensity factor and fracture energy determinations were made following a modified ASTM E399. The modification involved the use of a much smaller sample size than that called for by the ASTM test. This modification had been thoroughly investigated by Kenner and Jones (37-39) while at the Air Force Materials Laboratory. Sample size was 12.0 mm x 12.5 mm x 3.2mm. The sample clamping apparatus consisted of miniature clevis brackets having pins of 2.50 mm in diameter which fit into the compact tension sample pin holes leaving just enough room for free rotation of the pins. The miniature clevis brackets were threaded directly to 5/8 inch diameter steel shafts which were attached directly to the 1000 pound load cell and the Instron crosshead. The load cell was calibrated in the 10 Kilogram range and was found to have excellent linearity over all ranges used. A screw driven Instron tensile tester was used. The cross head speed was kept at .05cm per minute. The chart speed was kept at 10cm per minute. Fracture values were calculated using only the load at which crack propagation occurred from the initial inserted precrack. This was possible as a result of the constant crack tip radii of all of the compact tension samples tested (see appendix 1 for details of the precrack insertion technique) From the crack propagation load and geometric factors the critical stress intensity factor (KIC) and fracture energy (GIC) values were calculated from the equations below (ASTM E399).

$$K_{IC} = \frac{P_c F(a/w)}{BW^{1/2}}$$

$$G_{IC} = \frac{(K_{IC})^2}{E}$$



Where:
Pc = Crack propagation load (newtons)
E = Young's modulus (Pascals) (see appendix 3)
B = Sample thickness (Meters)
W = Sample dimension as labeled in figure 1. (Meters)
a = Crack length as labeled in figure 1. (Meters)
$F(a/W) = [(2+a/W)(0.886 + 4.64a/W - 13.32a^2/W^2 + 14.72a^3/W^3 - 5.64a^4/W^4)]/ [(1-a/W)]$
KIc and GIc values reported represent the mean values for all of the samples tested. The +/- values represent the standard deviation of the values from the mean.

This relationship between the critical stress intensity

factor (K_{Ic}) and the fracture energy (G_{Ic}) is an adaptation developed by Irwin (58) of the Griffith criteria for materials which plastically deform. The Griffith relationship is based upon the balance of the decrease in potential, stored elastic energy at a crack and the increase in surface energy resulting from growth of that crack. A crack will grow only when sufficient surface energy is supplied to the material. Griffith assumed the surface energy was equal to the product of the crack surface area and the specific surface energy of the material. Then applying the stress analysis of Inglis for a very sharp elliptical crack in an infinitely large plate of an elastic material, Griffith calculated the change in the potential, stored elastic energy of the plate due to the introduction of a crack to be:

$$U - U_o = -\frac{\pi\sigma^2 t a^2}{E} + 4at\gamma_s$$

Where; U_o = initial potential energy
U = the potential energy of the plate with a crack
σ = the applied stress
a = 1/2 the crack length
t = plate thickness
E = Young's modulus
γ_s = the specific surface energy

Differentiating U with respect to a yields:

$$\frac{\partial U}{\partial a} = 4t\gamma_s - \frac{2\sigma^2 at\pi}{E}$$

At equilibrium $\frac{\partial U}{\partial a} = 0$

Therefore at equilibrium $2\gamma_s = \frac{\pi\sigma^2 a}{E}$

Griffith rewrote this equation into the form:

$$\sigma = [2E\gamma_s / \pi a]^{1/2}$$

for plane stress, and:

$$\sigma = [2E\gamma_s / \pi a(1 - v^2)]^{1/2}$$

for plane strain where v = Poisson's ratio

Since most metals and polymers are not elastic up to the point of failure the fracture energy is usually much larger than the surface energy would predict. For these plastically deformable materials Irwin defined the elastic energy per unit crack length increment as G. He showed that:

$$= [E\ G/ \pi a]^{1/2}$$

G is know known as the fracture energy or the strain energy release rate, having units of energy per unit surface area.

G_{Ic} is the energy per unit surface area to cause the growth of a crack in tensile or Mode 1 opening.

APPENDIX C
Young's Modulus Measurements

Young's modulus was measured in three point bend configuration using the equations found in ASTM D790M. Sample dimensions were 12.0mm x 60mm x 3.2mm. A free standing screw driven Instron was used to perform the test. The cross head speed was maintained at .05cm per minute while the chart speed was maintained at 10cm per minute. The three point bent supports were flat surfaces with the central unit having a 4.8 mm diameter steel rod to apply the force to the beam. The three point bend span was 41.8 mm for all samples tested. A 1000 pound load cell was used in the measurement on the 10 kilogram scale. The deflection of the beam was calculated from the product of the crosshead speed and the time of deformation. The time of deformation was calculated from the chart speed and the distance traversed on the chart. Young's modulus is given by ASTM D790M as:

Young's Modulus $E = L^3M/4BD^3$ (Pascals)

Where:
L = Three point bend span (M)
M = The slope of the force deflection curve (Newtons/M of deflection)
B = Beam width (M)
D = Beam depth (M)

Only one beam sample was tested for each resin formulation, therefore no standard deviations are given for this parameter.

APPENDIX D
Dynamic Mechanical Analysis

The dynamic mechanical measurements were made on a Dynastat Dynamic Mechanical Tester manufactured by IMASS Inc.. The material parameters reported include the dynamic mechanical tensile storage and loss moduli and loss factor. All of the data was analyzed using the software supplied with the Dynastat.

The data reported in chapters 2 through 6 was taken on cured 60mm x 12mm x 3.2mm resin samples in a three point bend configuration. A 41.65mm three point bend span was used. The testing rig was supplied with the Dynastat. All experiments were run in load control mode. All non isothermal experiments were run at a constant heating rate of 2.4 degrees centigrade per minute. Data was taken for three frequencies (one, three,and five Hertz). All of the data reported in this dissertation is for one Hertz. The force and displacement functions were monitored constantly to maintain a clean sine wave. Beam deformation was kept to a minimum to satisfy beam theory assumptions.

The dynamic mechanical data in chapter 7 was taken on (10mm to 15mm) x 5mm x .1mm tensile films. The gripping apparatus was provided with the Dynastat. All experiments were run in load control mode. All non isothermal experiments were run at a constant heating rate of 2.4 degrees centigrade per minute. Data was taken at one, three and five Hertz. All of the data reported in this chapter is for one Hertz. The force and displacement functions were continuously monitored to maintain clean sinusoidal responses. Data was not corrected for any cross sectional area changes during cure.

APPENDIX E
Solvent Resistance Measurements

The resistance of the cured resin formulations to the absorption of distilled water, methylene chloride, methyl ethyl ketone, jet fuel JP5, deicing fluid, and Skydol hydraulic fluid (Montsanto product) was investigated by measuring the weight increase in samples immersed in these fluids at room temperature. These solvents were chosen from a Boeing specification for high performance composite matrix materials with aerospace applications. The immersed samples consisted of the broken halves of the fractured compact tension samples. Therefore all samples have the same approximate dimensions (12.5mm x 6.0mm x 3.2mm). The samples were fully immersed in 4 milliliters of solvent in 1 dram sample vials. When weighed the samples were handled only with forceps. When removed from the vials the samples were blotted dry. Care was taken to remove residual solvent from the drilled pin holes. The samples were then placed on the balance pan. For the less volatile solvents the weight recorded was that of equilibrium. Solvent evaporation during weighing was a problem for the methylene chloride and methyl ethyl ketone samples. For these samples the sample weight was taken as the highest weight observed after the perturbations due to sample application on the pan had died down. The weighing apparatus used was a Sartorious model R160D in the six decimal place mode.

APPENDIX F
Chemical Characterization

A). Elemental Analysis

Elemental analysis data was provided by the Analytical Service Department of the University of Massachusetts.

Fluorine analysis was accomplished using a Schoniger oxidation. The organic fluorine is burned in the presence of oxygen in a flask containing a platinum catalyst and water. The Fluoride anion produced dissolves in the water and is measured with a fluoride ion selective electrode which has been calibrated using knowns.

Nitrogen analysis was accomplished using a modified Dumas method. The organic nitrogen is burned in oxygen to give nitrogen oxide species. These nitrogen oxide species are then heated to 650 degrees centigrade in Helium in the presence of copper giving nitrogen gas. The nitrogen/helium gas mixture is passed across a Wheatstone bridge and an electrical potential is read between this Wheatstone bridge and one across which only helium is flowing. The electrical potential is calibrated with knowns.

B). Amine End Group Titration

All amine end group titrations were carried out by Owens Illinois Analytical Service, (Toledo, Ohio).

A non aqueous potentiometric titration for the amine end groups is carried out in a 25% solution of Acetic acid in methylene chloride. The polymer is dissolved in this solvent mixture after which the acetic acid is back titrated with Perchloric acid. This titration does not differentiate between primary and secondary amines.

APPENDIX G
Fracture Data

Table A7.1.

Mechanical Property Data for Resins Formulated Using An Amine Terminated Bisphenol A Polyaryletherketone of Mn = 4,400 and Amine termination Efficiency of > 85%

EPOXY RESIN	% MOD	AMINE	A/E	K_{IC} $N/M^{3/2}$	K_{IC} +/-	G_{IC} J/M^2	G_{IC} +/-
H69	0	DDS	1.2	$.88x10^6$	$.4x10^6$	257	22
H69	20	DDS	1.2	$1.2x10^6$	$.2x10^6$	409	130
H69	35	DDS	1.2	$1.5x10^6$	$.1x10^6$	682	120
H69	40	DDS	1.2	$1.5x10^6$	$.2x10^6$	712	148
E828	0	DDS	1.2	$.89x10^6$	$.05x10^6$	368	44
E828	25	DDS	1.2	$.91x10^6$	$.06x10^6$	343	44
E828	35	DDS	1.2	$1.1x10^6$	$.1x10^6$	499	105
E828	40	DDS	1.2	$1.2x10^6$	$.1x10^6$	520	125
MY720	0	DDS	1.2	----------			
MY720	25	DDS	1.2	$1.0x10^6$	$.1x10^6$	341	51

Table A7.2.

Mechanical Property Data for Formulations Using Two Higher Molecular Weight Amine Terminated Bisphenol A Polyaryletherketones of Mn = 7,000 and 21,000 having amine termination efficiencies of >83% and >80% respectively.

EPOXY RESIN	% MOD	AMINE	A/E	K_{Ic} $N/M^{3/2}$	K_{Ic} +/-	G_{Ic} J/M^2	G_{Ic} +/-
7,000 Mn BPAPK							
E828	0	DDS	1.0	$.89x10^6$	$.05x10^6$	315	35
E828	20	DDS	1.0	$1.6x10^6$	$.2x10^6$	905	202
E828	30	DDS	1.0	$1.8x10^6$	$.2x10^6$	1388	334
E828	40	DDS	1.0	$2.5x10^6$	$.1x10^6$	2344	184
21,000 Mn BPAPK							
E828	0	MDA	1.0	$.81x10^6$	$.1x10^6$	281	60
E828	10	MDA	1.0	$1.1x10^6$	$.07x10^6$	517	63
E828	20	MDA	1.0	$1.5x10^6$	$.07x10^6$	893	84
E828	25	MDA	1.0	$1.8x10^6$	$.13x10^6$	1350	198

TABLE A7.4 MECHANICAL DATA

RESINS FORMULATED USING A METHYLHYDROQUINONE PEEK OF Mn = 5,000 AND AN AMINE TERMINATION EFFICIENCY OF > 93%

EPOXY RESIN	PERCENT MODIFIER	K_{IC} $N/M^{3/2}$	K_{IC} +/-	G_{IC} J/M^2	G_{IC} +/-
E828	0	$.89x10^6$	$.05x10^6$	315	35
E828	10%	$.91x10^6$	$.06x10^6$	319	43
E828	20%	$1.0x10^6$	$.05x10^6$	359	37
E828	30%	$.97x10^6$	$.07x10^6$	403	59

TABLE A7.5

MECHANICAL DATA

RESINS FORMULATED USING A TERTIARYBUTYLHYDROQUINONE PEEK OF Mn = 3,200 AND AN AMINE TERMINATION EFFICIENCY OF > 91%

EPOXY RESIN	PERCENT MODIFIER	K_{Ic} $N/M^{3/2}$	K_{Ic} +/-	G_{Ic} J/M^2	G_{Ic} +/-
E828	0	$.89x10^6$	$.05x10^6$	315	35
E828	30%	$1.6x10^6$	$.03x10^6$	907	39
E828	40%	$1.6x10^6$	$.09x10^6$	877	106
H69	30%	$1.5x10^6$	$.11x10^6$	737	108
H69	40%	$1.9x10^6$	$.05x10^6$	1,104	66

RESINS FORMULATED USING A TERTIARYBUTYLHYDROQUINONE PEEK Mn = 4,600

E828	30%	$1.5X10^6$	$.08x10^6$	883	93
E828	40%	$1.9X10^6$	$.04x10^6$	1,277	57

TABLE A7.6

RESINS FORMULATED USING A RESORCINOL PEEK OF Mn = 3,400 AND AMINE TERMINATION EFFICIENCY OF > 92%

EPOXY RESIN	PERCENT MODIFIER	K_{Ic} $N/M^{3/2}$	K_{Ic} +/-	G_{Ic} J/M^2	G_{Ic} +/-
E828	0	$.89x10^6$	$.05x10^6$	315	35
E828	30%	$1.1x10^6$	$.12x10^6$	433	93
E828	40%	$1.2x10^6$	$.03x10^6$	529	28

RESINS FORMULATED USING A RESORCINOL PEEK OF Mn = 7,000

E828	30%	$1.0X10^6$	$.05x10^6$	395	38
E828	40%	TOO VISCOUS TO PROCESS			

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